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(IZVESTIYA AKADEMII NAUK SSSR)

(OTDELENIE KHIMICHESKIKH NAUK)

IN ENGLISH TRANSLATION

$$\frac{c}{b}$$

CONSULTANTS BUREAU

SYNTHESES OF HETEROCYCLIC COMPOUNDS

Edited by
A. L. MNDZHOIAN

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Table should be changed to

Pressure Dependence of Rate Constant ($t = 50°$)

P in kg/cm^2	$k_1 \cdot 10^4$ in liter $\cdot$ mole$^{-1} \cdot$ min^{-1}
1	8.80
500	13.2
1000	18.7
2000	32.8

THE EFFECT OF THE GASEOUS MEDIUM ON THE COURSE OF PHYSICO-CHEMICAL PROCESSES IN SEMI-CONDUCTING OXIDES AT HIGH TEMPERATURES

A. I. Leonov

Institute of the Chemistry of Silicates, Academy of Sciences of USSR

In the investigation of reaction kinetics in solid phases, great importance attaches to a study of the conditions in which the stoichiometry of chemical compounds can be disturbed, since their reactivity depends upon this [1,2]. One of the factors which affects deviation from stoichiometric ratios in oxides is the gaseous medium. For example, on reducing the partial pressure of oxygen in the atmosphere, there may take place a partial evolution of oxide from the solid into the gaseous phase, so that an excess of metal atoms appears in the oxide. In such "defective" substances physicochemical processes may take place with great velocity. An increase of the reactivity of oxides may also be produced as a consequence of chemical adsorption of oxygen, and the formation of nonstoichiometric surface compounds. There has recently been a growth of interest in the study of the part played by deviations from stoichiometry in the chemistry of solid bodies at high temperatures. In 1957 the results were published of investigations of the properties of refractory oxides such as thorium dioxide, chromium oxide (Cr_2O_3) and zirconium dioxide [3], as well as uranium dioxide [4], on heating to 2000°, in a vacuum, and in atmospheres of argon, carbon monoxide, and other gases.

Results are given in the present article of a study of the reactivities of zinc oxide and the chromium oxide (Cr_2O_3) in relation to the partial pressure of oxygen in the gaseous phase. The experimental data obtained on the reaction kinetics and the sintering of the oxides, are compared with the existing data on the catalytic and electrical properties of the oxides. A general relationship is observed between the reactivity, the catalytic activity and the electrical conductivity of semi-conducting oxides and the composition of the gaseous phase.

EXPERIMENTAL

The starting materials were oxides of brand "Pure for Analysis". The samples were heated to 1500° in a platinum oven, and to temperatures above 1500° in a molybdenum tube furnace. The gaseous media used were air, argon, hydrogen and metal vapors. Table 1 gives the partial pressures of oxygen in the gases used.

TABLE 1

The Partial Pressures of Oxygen in Gases at Various Experimental
Temperatures

Gaseous medium	P_{O_2} in atm		
	1000°	1500°	1750°
Air	0.21	0.21	0.21
Argon containing 0.4% oxygen	$4.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$
Hydrogen containing 2.3% water	$1.7 \cdot 10^{-18}$	$1.1 \cdot 10^{-12}$	$7.4 \cdot 10^{-11}$

The quantitative determination of the chemical compounds present in the oxide mixtures after heating was accomplished with the help of chemical phase analysis. In analysis of the mixture zinc oxide-aluminum oxide [5], the method used was selective dissolution of the zinc oxide in hydrochloric acid (1:1) at room temperature; zinc aluminate, $ZnAl_2O_4$, and alumina remained in the residue. For analysis of the roasted mixture of magnesia and chromic oxide, the free magnesia was dissolved in a 10% ammonium nitrate solution with heating; magnesium chromate, $MgCr_2O_4$, and chromic oxide remained in the residue. The determination of the quantity of the dissolved components was performed with the help of complexometric titration [6]. The phase composition of the substances investigated was also determined by means of x-ray and microscopic analyses. The sintering of the samples was characterized by means of the following indices: linear shrinkage, porosity, volume-weight and specific gravity.

The reaction $ZnO+Al_2O_3 = ZnAl_2O_4$. The zinc oxide and the alumina were previously roasted for two hours at 1000°, and ground in a mortar to a fineness corresponding to a 200 mesh sieve. Experiments were carried out at temperatures of 900°, 950° and 1000°, in argon containin g 0.4% oxygen, in pure argon, and in the vapor of metallic zinc. The argon was purified from oxygen by passing it through a tube furnace filled with shavings of metallic magnesium, at a temperature of 600°. Experiments in the vapor of metallic zinc were carried out in the following way. The zinc and the sample under investigation were introduced into a quartz test tube as shown in Fig. 1. The tube with its contents was placed in a furnace and heated. The zinc which was contained in the base of the tube, was evaporated, and the vapor moved upwards and was condensed on the walls of the tube, from which the metal then drained off downwards. During the course of the experiment, the atmosphere contained zinc vapor at a pressure of a few mm of mercury (when the zinc was melted at a temperature of 500-600°). The results of these experiments are given in Table 2.

TABLE 2

Influence of Gaseous Medium on the Course of the Reaction
$ZnO+Al_2O_3 = ZnAl_2O_4$

Tempera- ture in °C	Period in minutes	Quantity of $ZnAl_2O_4$ produced in %		
		argon+ 0.4% oxygen	purified argon	metallic zinc vapor
900	60	5,5	12,0	23,0
950	60	20,0	60,5	59,5
1000	60	35,0	89,7	88,2

It can be seen from Table 2 that the formation of zinc aluminate proceeds 2-3 times more quickly in purified argon and in zinc vapor, as compared with its rate in argon containing 0.4% oxygen.

According to published data [2], deviation from the stoichiometric composition in zinc oxide occurs with change in atmospheric composition. It would therefore be desirable to trace the change in the metal to oxygen ratio in the oxide which occurs with change in the partial pressure of oxygen. However, such an analysis presents difficulties, since the quantitative change in the composition is very small, and since this change takes place preferentially at the boundaries of the crystals and the aggregates. A practical solution of this problem can only be realized by investigating new methods of physicochemical analysis.

The reaction $MgO+Cr_2O_3 = MgCr_2O_4$. The formation of chromspinel has been the subject of many investigations [7], because of the value of this compound as one of the phases entering into the composition of chromomagnesite refractories. In the course of the investigations, the great velocity with which magnesium chromate is formed, in comparison with that with which magnesium aluminate is formed, has been noted, and has been explained by the greater mobility possessed by the chromium atoms in comparison with those of aluminum. The investigations referred to have been conducted in an atmosphere of air, that is, in an oxidizing medium. It is of technical interest to carry out an investigation of the kinetics of the formation of magnesium chromate in gaseous media at various partial pressures of oxygen, since the basic refractories used in metallurgical furnaces are subject to the influence of a gaseous atmosphere containing varying concentrations of oxygen.

In experiments carried out to investigate the synthesis of chromspinel at 950° and 1000°, the finely dispersed mass I (Table 3) was used, possessing particle size less than that of a 200 mesh sieve. At temperatures of 1350° and 1500°, in view of the large rate of formation of chromspinel, the experiments were carried out with the coarser dispersion II, which passed through a 95 mesh sieve. The results of these experiments are presented in Table 3.

TABLE 3

Effect of the Gaseous Medium on the Course of the
Reaction $MgO + Cr_2O_3 = MgCr_2O_4$

Temperature in °C	Period in minutes	Quantity of magnesium chromate formed in %			Number of sample
		air	Ar + 0,4% O_2	H_2 + 2,3% H_2O	
950	30	67,0	53,6	35,0	I
1000	30	80,0	69,2	52,5	I
1350	60	82,5	51,7	85,0	II
1500	60	91,0	—	96,0	II
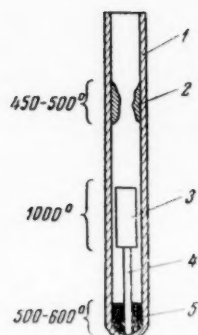
Fig. 1. The quartz tube used in experiments on zinc vapor: 1) quartz tube; 2) sublimated zinc; 3) specimen; 4) support; 5) zinc.

It is seen from Table 3 that, at 950° and 1000°, the quantity of chromspinel formed increases with increase in the oxygen concentration in the gas phase. This is explained in the following way: chromium forms with oxygen a series of oxides: CrO_3, Cr_5O_{13}, Cr_5O_{12} and Cr_2O_3, which may exist within definite temperature limits [8]. Above 400° the stable form is Cr_2O_3. At higher temperatures, however, chemical adsorption of oxygen is observed [9], as a result of which surface oxygen compounds of chromium are formed, in which the chromium has an increased valence. At 1350° when the partial pressure of oxygen is reduced from 2.1×10^{-1} atm (air) to 4×10^{-3} atm (argon + 0.4% oxygen), the quantity of magnesium chromate formed is reduced from 82.5% to 51.7%, which may be connected with the desorption of oxygen present in excess of the stoichiometric composition. Further reduction in the oxygen pressure, however, down to $\sim 10^{-13}$ atm (hydrogen), causes an increase in the yield of magnesiochromite to 85%. Under high temperature conditions (1350°), dissociation of the chromic oxide commences in an atmosphere of hydrogen: $Cr_2O_3 = 2Cr + 1.5\ O_2$ as a result of which part of the oxygen is transferred to the gas phase, while in the solid phase, an excess of chromium atoms arises. With increase in temperature, the dissociation phenomenon is revealed very clearly, as can be seen from the experiments on the synthesis of magnesium chromite at 1500° given in Table 3, and those on the sintering of chromic oxide at 1750° (Table 4).

It is seen from Table 4 that the greater contraction of the chromic oxide samples in an atmosphere of argon is associated with a reduction in the porosity. Crystals are not discovered in those specimens which are roasted in air; the samples possess scattered, very fine pores, Those samples which are roasted in argon are coarsely crystalline, with crystal dimensions reaching 50μ.

TABLE 4

Sintering of Chromic Oxide (Temperature = 1750°, Duration of Roasting = 3 hours)

Index of sintering	Atmosphere	
	air	Ar + 0,4% O_2
Linear shrinkage, %	3,5	17,5
Volume weight in g/cm^2	3,04	4,62
Specific gravity in g/cm^2	5,38	5,37
Apparent porosity %	38,60	1,40
True porosity %	43,60	13,96

As the experiments under consideration have shown, physico-chemical processes may be activated in the oxides at high temperatures, by changing the partial pressure of oxygen in the gas phase.

The General Nature of the Effect of the Gaseous Medium on the Reactivity, Catalytic Activity and Electrical Conductivity of Semiconducting Oxides.

At the present time a theory is widely accepted [10-13], according to which electronic processes which are developed in semiconductors and which determine their electrical and magnetic properties, also determine their reactivity and their catalytic activity. It is therefore a matter of interest to compare the experimental data which we have obtained on the influence of the gaseous medium on the kinetics of chemical reactions, the sintering and the recrystallization of oxides, with data on the electrical conductivity and the catalytic activity of the same oxides in relationship to composition of the gaseous medium.
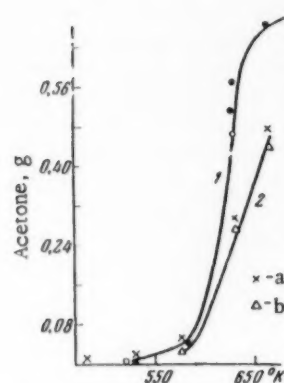
Fig. 2. Yield of acetone after two hours in relationship to the temperature: 1) in pure nitrogen; 2) in a mixture of nitrogen with 0.4% oxygen, due to the dehydrogenation reaction: a) based on the quantity of acetone; b) based on the quantity of hydrogen. After Myasnikov and Pshezhetskii.

Zinc oxide. The extent to which the reaction: $ZnO + Al_2O_3 = ZnAl_2O_4$ proceeds at temperatures of 900°, 950° and 1000°, increases by a factor of 2 or more in argon or in zinc vapor in comparison with that in argon containing 0.4% oxygen, as has been shown in Table 2. Myasnikov and Pshezhetskii [14] have investigated the connection between the catalytic and the semiconducting properties of zinc oxide. They investigated concurrently the electrical conductivity of zinc oxide, and its catalytic activity in the dehydrogenation of isopropyl alcohol with the formation of acetone. The electrical conductivity of the zinc oxide was measured in the course of the reaction. The experiments were carried out in atmospheres of pure nitrogen and hydrogen, and also in mixtures of gases (nitrogen + 0.4% oxygen, and hydrogen + 3% oxygen). Fig. 2 gives the curves which represent the relationship between the quantity of acetone formed after two hours, and the temperature. Comparison of curves (1) and (2) shows that the presence of 0.4% oxygen reduces the rate of the reaction at 300° by a factor of 2 once again. Fig. 3. gives curves for the temperature dependence of the electrical conductivity of zinc oxide, measured in the course of these experiments. It is seen from this figure that the electrical conductivity of the zinc is diminished in the presence of oxygen, depending on the temperature, by a factor between 2 and 5. Similar results were obtained in experiments using an atmosphere of hydrogen, and a mixture of hydrogen with 3% oxygen.

The existence of a general relationship between the reactivity, electrical conductivity and catalytic activity of zinc oxide, and the composition of the gaseous medium shows that the same reason lies behind the activation of these processes. Myasnikov and Pshezhetskii suggest that the change in the properties of the zinc oxide consists of change in the concentration of electrons in the conductivity zone or in the concentration of the inter-lattice zinc ions. According to current opinions [1,2], change in the partial pressure of oxygen in the atmosphere causes an alteration in the ratio between the zinc and the oxygen atoms in the solid oxide, as a result of which the energy of the interatomic bonds is changed, and, correspondingly, a change takes place in the properties of the zinc oxide. The problem of the chemical bond is a fundamental one in the chemistry of semiconductors (approximate order) [15].

Chromic oxide. The reaction $MgO + Cr_2O_3 = MgCr_2O_4$ proceeds at 950° to the extent of 35% in hydrogen, of 53.6% in argon, and of 67% in air (Table 3). The quantity of chromspinel formed can therefore be seen to increase with increase in oxygen concentration in the gas phase. It is seen from Fig. 4. that the same relationship is observed for the electrical conductivity of chromic oxide in relation to the oxygen pressure [16]. The reactivity and the electrical conductivity of chromic oxide change parallel to each other. At higher temperatures the reverse relationship is observed: the reactivity (Table 3), the sintering (Table 4) and the overall recrystallization of the chromic oxide increase with reduction of partial pressure of oxygen in the gas phase. No experimental data on the electrical conductivity of chromic oxide at high temperature (1350°-1750°) are available. It may be supposed that the electrical conductivity of chromic oxide has the same complex temperature relationship with the concentration of oxygen as the reactivity of this oxide.
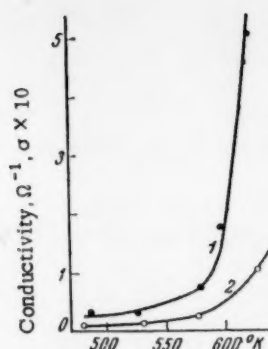
Fig. 3. Change in the conductivity of zinc oxide with temperature in the reaction zone: 1) in pure nitrogen; 2) in a mixture of nitrogen with 0.4% oxygen. After Myasnikov and Pshezhetskii.

Fig. 5. Relationship between the electrical conductivity of titanium dioxide and the oxygen pressure: 1) 300°; 2) 900°; 3) 1000°. (k is given in ohm^{-1} cm^{-1}; k = p_{O_2} in mm Hg). According to Hauffe, Tränckler-Greese, and Grünewald.

Fig. 4. Relationship between the electrical conductivity of chromic oxide and the oxygen pressure at 800° (k is given in ohm^{-1} cm^{-1} and p_{O_2} is given in mm Hg). After Hauffe and Block.

Titanium dioxide. We have carried out experiments involving the heating of specimens of titanium dioxide at temperatures of 1350° and 1550° for a period of two hours. The roasting has been carried out in air and in argon. At 1350° the linear shrinkage of the samples in air amounted to 18.2%, and in argon to 20.7%. The overall recrystallization of the titanium dioxide took place to a greater extent in argon than in air. The dimensions of the crystals when roasting was performed at 1550° in argon amounted to 180μ and those when the heating was performed in air to 60μ. In the samples roasted in argon, there was observed, around the periphery and the boundaries of the granules, the formation of a phase defective in oxygen. The samples had a dark blue color.

In a paper by White [2] it is stated that, when samples of titanium dioxide are heated in air to a temperature a little above 1500°, they take on a dark blue color and become semiconducting. It can be seen from Fig. 5. that the electrical conductivity of titanium dioxide increases with reduction in the oxygen pressure [17]. Deviation from stoichiometric composition in the case of titanium dioxide causes intensification in the oxide of the sintering process and of the overall recrystallization, with simultaneous increase in the electrical conductivity.

CONCLUSIONS

1. An investigation has been made of the effect of oxygen pressure on the kinetics of the reactions: $ZnO + Al_2O_3 = ZnAl_2O_3$ and $MgO + Cr_2O_3 = MgCr_2O_3$.

2. Experimental confirmation has been produced for the general nature of the effect of the gaseous medium on the course of certain physico-chemical processes: for zinc oxide by comparing the reactivity, the catalytic activity and the electrical conductivity; for chromic oxide by comparing the reactivity and electrical conductivity; and for titanium dioxide by comparing the overall recrystallization the sintering and the electrical conductivitiy.

3. The kinetics of the physico-chemical processes considered are based upon deviations of the composition of semi-conducting oxides from the stoichiometric composition, as a result of the dissociation of the oxides or the adsorption of oxygen by them.

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AN INVESTIGATION OF THE ADSORPTION OF VAPORS
ON ADSORBENTS POSSESSING A NONUNIFORM SURFACE

PART 2: EXPERIMENTS WITH ORGANIC-SUBSTITUTED SILICA-GELS

L. G. Ganichenko, M. M. Dubinin, E. D. Zaverina,

V. F. Kiselev and K. G. Krasil'nikov

Institute of Physical Chemistry of the Academy of Sciences of USSR,
and the M. V. Lomonosov Moscow State University

The successive stages in the investigation of the adsorption of various vapors on nonuniform surfaces have consisted of adsorption measurements on hydrophobic organic-substituted silica-gel. Chemical modification of the silica surface, by substituting its hydroxyl groups by organic radicals has been repeatedly investigated [1-10]. Various methods exist for obtaining organic-substituted silica-gels. Investigations of the irreversible sorption of methanol vapor on silica-gel [1], aluminosilicates and alumina-gel [10-11] show that even at low temperatures part of the most active hydrosilic groups of the surface are replaced by methoxy-groups. This process takes place most completely at higher temperatures and pressures [12]. Different methods for methoxylation of the surface of silica and silicates are described in other publications [2,5,8,9,12]. In the course of this process, surface esters are formed, which, like their volume analogues, are unstable compounds and are comparatively easily hydrolyzed on contact with water.

The Si-R bonds in substituted silanes are more stable. The direct synthesis of such compounds on the surface of silicate adsorbents presents considerable difficulty [2]. If, however, one starts with substituted silanes, containing organic radicals and groups, these groups being capable of exchange reactions with the hydroxyls of the surface, then chemical adsorption of such substances on the silica may lead to the production of the corresponding surface compounds. In previous work [4,6,9,13], methylation and phenylation of silica-gel has been carried out. This process of obtaining organic-substituted silicas by grinding its various modifications in the presence of organic compounds, is most important, when the free radicals developed by its disintegration are replaced by organic groups [7].

The results of the investigations of the adsorptive properties of organic-substituted silicas show an appreciable reduction of the adsorption of water vapor [6,9,13], methanol vapor [5], ammonia [6], and ethylene [9] in comparison with the initial samples. The substitution of the surface hydroxyl groups of silica-gel by methoxy- and methyl-groups may be carried out practically completely. According to the data which have been obtained in the investigation of infra-red absorption spectra for methoxylated and methylated silica-gels, the intensity of the bands corresponding to the fundamental frequency of the free oscillations of the hydroxyl groups is reduced, and for certain samples is completely lacking [8,9].

The effect of the chemisorption of alkyl- or arylchlorosilanes may be a considerable modification of the structure of the silica-gel. Measurements of the specific surface of the initial silica-gel, and of silica-gel which has been subjected to prolonged treatment by chloromethylsilane, show that the accessible specific surface is

diminished by a factor greater than 10 [9]. It would seem that the porous structure of the gel undergoes considerable change as a result of the growth in its surface layer during this process, such as, for example:

$$>Si<\begin{array}{c}CH_3\\CH_3\end{array}$$
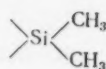
In order to study in an uncomplicated form the effect of the nature of the surface on the adsorption of vapor, adsorption measurements should be carried out on non-porous adsorbents, or on coarse-pored adsorbents with uniform pore-structure, referring the adsorption magnitudes obtained to unit surface area. It is necessary to determine the specific surface from the adsorption isotherm of vapors which effectively do not affect the chemical nature of the adsorbent surfaces. It is common to use nitrogen as such a material.

In the present communication we give the results of an investigation of the adsorption of various vapors on methylated coarse-pored silica-gel, and on a demethylated specimen obtained from it under conditions in which it is very improbable that any substantial change in it specific surface would occur.

EXPERIMENTAL

1. The inital sample consisted of a coarse-pored technical silica-gel of brand KSK, which was carefully purified from impurities of iron and other materials. In order to methylate the silica-gel surface in a vacuum, it was submitted to repeated treatment by dichlorodimethyl-silane vapor at 200°. After the treatment the silica-gel was evacuated in a vacuum plant at 100°, and afterward washed with water until it gave a negative reaction for chloride ions. In what follows we shall use the symbol S-1 for the silica-gel methylated in this way. A separate portion of silica-gel S-1 was treated with nitric acid vapor at 200° for 6 hours. The effect of this was to bring about oxidation of the organic constituent of the surface, the methyl radicals were replaced by hydroxyl groups, and the methylated silica-gel, which now possessed hydrophilic properties, became hydrophilic in its behavior. This sample was denoted by S-2. It appears that there is no effective change in the size of the surface under such treatment, a fact which we have repeatedly arrived at for similar cases, such as the regeneration and purification of silica-gel by nitric acid vapor from residual quantities of organic substances adsorbed by them. It is impossible to decide what quantity of hydroxyl-groups remain on the surface of the organic substituted silica from the data obtained during diazomethylation of the sample [9], since, according to [5,14], this method gives only ~ 30% of all the hydroxyl groups, determined by the loss in weight under ignition. We have therefore determined the composition of the surface of silica-gels S-1 and S-2 on the basis of organic analysis carried out, together with determination of weight loss on ignition to 1250°. The analytical results are given in Table 1. In the same table are presented the magnitudes of the specific surfaces of the silica-gels investigated, as determined on the basis of the low temperature adsorption of nitrogen vapor by the BET method (see Table 3).

TABLE 1

Structural Water Content and CH_3-Groups in Samples of Silica-Gel.

Sample	Temp. of previous treatment °C	s, m²/g	CH_3 μ mole / g	Structural water μ mole/g
KSK-3	300	340	0	4,13
S-1	100	204	9,8	4,63
S-2	100	210	0	5,1

It can be seen from Table 1 that the demethylation of the surface led to some increase in its degree of hydration. The specific surface of the specimen, however, was only altered by 3%.

As in the previous work [14], we have used as substances for adsorption, nitrogen, cyclohexane, benzene and water. The adsorption of nitrogen at -195° was determined in a volume apparatus [15], while the adsorption of the remaining substances was measured according to the method of sorption-weight (see, for example, [16]). The preliminary evacuation of the adsorbents was carried out at a temperature of 150°.

2. Figures 1-4 give the sorption branches of the adsorption isotherms obtained for nitrogen, and for cyclohexane, benzene and water vapor. In all cases the isothermal curves for methylated silica-gel S-1 are situated lower than those for the demethylated silica-gel S-2. The difference between the adsorption properties observed for nitrogen was considerably smaller. The magnitude of the adsorption a_m, determined from the BET adsorption isotherms corresponding to the formation of a uniform unimolecular layer of nitrogen, amounted to 2.16 mM/g for silica-gel S-2 and 2.08 mM/g for silica-g S-1. These results are even closer together, from which it may be concluded that the specific surfaces of silica-gels S-1 and S-2 are practically identical.
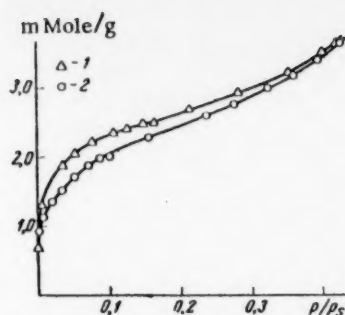
Fig. 1. Adsorption isotherms for nitrogen vapor at -195° for silica-gels: S-2 (1) and S-1 (2).
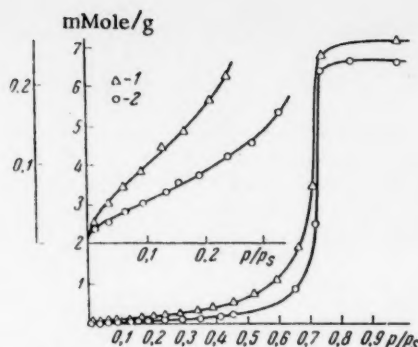
Fig. 2. Adsorption isotherms of cyclohexane vapor at 20° for silica-gels: S-2 (1) and S-1 (2).
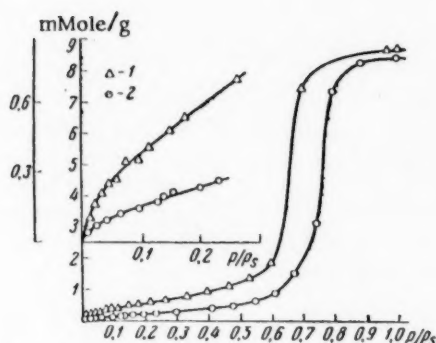
Fig. 3. Adsorption isotherms for benzene vapor at 20° for silica-gels: S-2 (1) and S-1 (2).
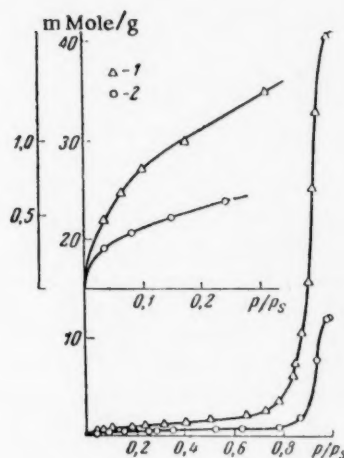
Fig. 4. Adsorption isotherms for water vapor at 20° for silica-gels: S-2 (1) and S-1 (2).

TABLE 2

Limiting sorption volumes

Vapor	C_6H_{12}		C_6H_6		H_2O	
Sample	$\frac{m}{mole/g}$	cm^3/g	$\frac{m}{mole/g}$	cm^3/g	$\frac{m}{mole/g}$	cm^3/g
S-1	6,94	0,748	8,45	0,752	12,13	0,218
S-2	7,21	0,780	8,70	0,773	40,36	0,727

Compairson of the magnitudes of the limiting sorption volumes v_s (Table 2) for cyclohexane, benzene and water shows that for the first two substances, the magnitude v_s is changed only slightly in moving from silica-gel S-1 to sample S-2. Demethylation of the surface of the silica-gel does not increase significantly the limiting sorption volume of the sample.

For adsorption of water vapor on the more hydrophobic silica-gel S-1, however, the magnitude of the limiting sorption volume lies considerably lower than for the other substances. The same has been observed earlier, also, for the sorption of water vapor on a fluorinated specimen of silica-gel. It is quite possible that this difference is due to the fact that the walls of the pores of the hydrophobic silica-gel S-1 are not wettable by water.

The magnitudes of the limiting sorption volumes of cyclohexane and benzene, and of the specific surfaces determined from the adsorption isotherms of nitrogen, increase in moving from sample S-1 to sample S-2 by

only 3-6% in all. It appears, therefore, that the observed difference in the magnitudes of the adsorption are essentially due to chemical modification of the surface. Similar results were obtained in previous work [13-14].

DISCUSSION OF THE EXPERIMENTAL RESULTS

It is known [17,18] that the silica surface is nonuniform, and consists of siloxane and silanol portions, which possess different activation energies [17,19]. The degree of hydration of the surface, determined by the number of free angles in the silico-oxygen tetrahedra is not connected with the space structure, but depends on crystallo-chemical peculiarities of the structure of the sample surface [21], the conditions of its treatment, and other factors [20-22]. When interaction occurs between the elements of the hydrated portion of the silica-gel surface.

$$
\begin{array}{cc}
\text{OH} & \text{OH} \\
| & | \\
-\text{Si} - \text{O} - \text{Si} - \\
| & |
\end{array}
\tag{I}
$$
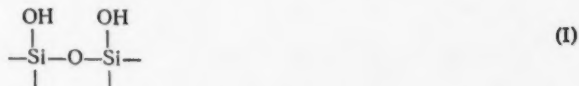
with monomers of dimers of the dimethyldichlorosilane molecule, the formation of the following surface compounds is possible:

(II)   (III)   (IV)
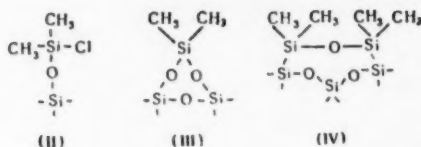
Cases (III) and (IV) have been considered in publication [6].

According to the data given in Table 1, in moving from the initial silica-gel sample KSK-3 to the methylated sample S-1, the content of structural water per unit surface is not only not reduced, but has a tendency to a certain increase. This is in part due to the appreciably lower temperature at which silica-gel sample S-1 undergoes its previous treatment, which could result in some quantity of adsorbed water remaining on its surface. On the other hand, this shows that the larger part of the surface of the hydroxyl groups of the initial silica-gel is replaced by silico-organic radicals according to scheme II, which after treatment of the silica-gel by water does not generally lead to any change in the number of hydroxyl groups per unit surface.
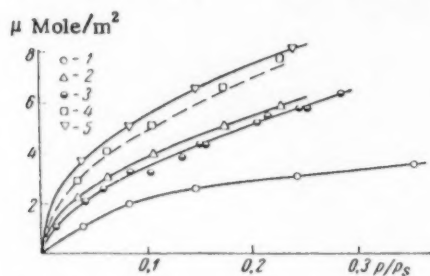
Fig. 5. Adsorption isotherms for water vapor at 20° (the magnitude of the adsorption is related to unit surface of the adsorbent) for silica-gels: S-1 (1), S-2 (2), KSK-2 (3): The specific surfaces are determined from the low temperature adsorption of nitrogen. S-1 (4) and S-2 (5): The specific surfaces of these are determined from the adsorption isotherms of water, which is taken to have a molecular area $\omega = 26$ A^2. The dotted curve depicts the absolute adsorption isotherm of water vapor on a hydrated coarse-pored silica-gel according to [24].

When the silica-gel S-1 is demethylated, that is, when all its methyl groups are replaced by hydroxyl groups, the content of structural water is only slightly increased (see Table 1). This seems to show that the demethylation of the surface of silica-gel S-1 at 200° causes a part of the neighboring hydroxyl groups to condense together, with the elimination of water and the formation of siloxane portions on the surface.

Investigation of the adsorption of water vapor on a thermally dehydrated sample of silica shows that, on the initial part of the isotherm, the magnitude of the adsorption depends basically on the degree of hydration of the surface [20,23-26]. At a relative pressure of 0.1 this relationship is practically linear [26]. The adsorption and energetic properties of the surface depend, however, not only on the number of adsorption centers, but also on the topography of the surface. When the distance between neighboring hydroxyl groups is small, the latter may undergo mutual interaction with the formation of hydrogen bonds, and the energetic properties of the surface may be reduced [19,27,28]. In addition to this, the nature of the arrangement of the hydroxyl groups on

the surface, which is dependent on the different orientations of the surface tetrahedra of SiO_4, may affect the ratio between the number of adsorbed molecules and the number of hydroxyls on the surface [26]. For different degrees of covering of the surface by water molecules, these may form 1 to 4 hydrogen bonds with the surface [29].

It appears from Fig. 5, that the adsorption isotherm of water vapor on the methylated specimen S-1 lies considerably lower than the isotherm on silica-gel KSK-2 which was investigated in work [26], the latter possessing approximately the same value of surface hydration (4, 12 μMole/g). It appears that, although the concentration of hydroxyl groups on the surface is the same, their arrangement on the surface of silica-gel S-1 is such that part of them are inactive with respect to water adsorption. A similar observation was made in work [6]. According to these data, when 38% of all the hydroxyl groups are replaced by methyl groups, the adsorption of water in the monolayer region is diminished by a factor of 10, while the adsorption isotherm of ammonia on this sample is practically the same as that for a sample which has been strongly dehydrated at 800° and, according to the data obtained by the author, practically contains no hydroxyl groups. The dehydration of the surface, both by thermal treatment and by substituting part of the hydroxyl groups by methyl groups, apparently produces not only a reduction of the concentration of groups on the surface, but also a change in their topography.

It is possible that the reduction in the adsorption power by thermal dehydration of the silica-gels, and the change of the adsorption isotherm of water vapor from convex to concave [23,25,26], is due to the fact that the linkage between the water molecules and the neighboring hydroxyl groups is a more probable event than the formation of isolated hydrogen bonds with the separately situated isolated hydroxyl groups [22]. It may be that this is one of the reasons for the low adsorption power of methylated silica-gel S-1. A portion of the molecules of dimethyldichlorosilane may be linked to the surface in accordance with scheme (II); and the formation of hydrochloric acid when silica-gel S-1 is treated with water and evacuated under high vacuum is in favor of this suggestion. The result of this is the formation on the surface of additional hydroxyl groups, situated sufficiently close to each other to be capable of combining amongst themselves by means of the hydrogen bond, which will also lead to a reduction in the adsorption powers of the surface [19, 28]. When the silica-gel is demethylated, the methyl groups of formulas (II) - (IV) are replaced by hydroxyl groups, and some of them, apparently, condense amongst themselves with the elimination of water and the formation of siloxane portions on the surface. The adsorption power of the silica-gel with respect to water and to benzene, which is linked with the hydroxyl groups by means of acceptor-donor interaction [30], increases because of this. It is interesting to note the considerable sensitivity of the adsorption of cyclohexane to change in the nature of the surface, which has also been observed in experiments with fluorinated silica-gels [14].

TABLE 3

BET Equation Constants for the Silica-Gels Studied

Vapor	Silica-gel S-I			Silica-gel S-II		
	a_m, mMole/g	c	Interval h	am, mMole/g	c	Interval h
N_2	2,08	62,6	0,05 —0,38	2,16	166	0,035—0,40
$C_f H_{12}$	0,144	4,26	0,125—0,32	0,279	4,25	0,08—0,27
$C_6 H_6$	0,295	7,22	0,10 —0,40	0,632	11,1	0,07—0,35
H_2O	0,482	33,3	0,04 —0,32	1,01	22,0	0,03—0,40

The results of a previous investigation [14] and previously published data [19, 26], show that, notwithstanding the nonuniformity of the surface on the molecular scale, and the discreteness of the location of the adsorption centers, the BET polymolecular adsorption equation is formally adequate for the description of the adsorption of a series of substances on such surfaces within the usual interval (0.05-0.35), or within a somewhat restricted interval of relative pressure. In the case which we are considering, the adsorption isotherms for all the investigated vapors on silica-gels S-1 and S-2 corresponds well to the BET equation. Because of this it has been possible to calculate the constants a_m and c for this equation for all the vapors investigated. Table 3 gives the value of these constants and the relative pressure intervals $h = p/p_s$ within which the BET equation corresponds to the experi-

mental data. For all the vapors, as well as for fluorinated specimens [14] the corresponding values of the equilibrium pressure for the adsorption a_m.

$$h_m = \frac{\sqrt{c}-1}{c-1}$$

are found to lie within the intervals given in Table 3 for the application of the equation. The values of h_m lie somewhat higher for cyclohexane. It appears from Table 3 that the nature of the change of the constant a_m, in moving from silica-gel S-1 to S-2, is basically in harmony with the change of the adsorbability of vapors described above, and is the result of chemical modification of the surface. This change is only very weakly expressed in the case of nitrogen. This correspondence is less regular for the constant $\underline{c}$.

The calculation of the specific area of the surface is subject to some uncertainty, not only on account of the calculation of the capacity of the unimolecular layer, a_m, from the BET equation, but also to a greater degree on account of uncertainty in the choice of the molecular area ω in a completely filled unimolecular layer. The latter depends to a considerable degree on the packing of the molecules in the surface layer. In papers [26, 31] it has been shown that, in the case of adsorption which is specific to the change in the chemical nature of the surface, the latter exercises a considerable influence on the orientation of the molecules in the surface layer. In order to estimate the molecular area ω of the vapor under consideration, in a completely filled unimolecular layer, on the basis of the BET equation, it is necessary to suppose that the molecular area of nitrogen, ω_{N_2}, is independent of the nature of the surface. This assumption is, of course, conditional. However, the results of previous investigations [14] show that the adsorption of argon and nitrogen, on the assumption of a constant value for the molecular area of the nitrogen, give values for the molecular area of the argon which do not differ by more than 7% for the initial silica-gel, and for fluorinated silica-gels differing in the chemical non-uniformity of their surfaces. Consequently, in the reverse case also, if it were postulated that the molecular area of the argon is constant, then the change in the molecular area of nitrogen would be the same. It seems, therefore, that we may within this degree of accuracy postulate constancy for the molecular area of nitrogen, and take it for our present work as equal to 16.2 A^2. Evidence is also provided in [15] for the small effect which the nature of the surface exercises on the adsorption of nitrogen vapor, within the limits for which the BET equation is applicable. The values for the molecular areas of all the vapors investigated, on these assumptions, are given in Table 4. The vlaues of a_m necessary for these calculations are taken from Table 3.

TABLE 4

Magnitude of Molecular Areas for Complete Unimolecular Layers

Substance being adsorbed	ω $\overset{\circ}{A}{}^2$	
	S-1	S-2
H_2O	70	34,5
C_6H_6	114	55,2
C_6H_{12}	234	125

It appears from Table 4 that the molecular areas are changed substantially by chemical modification of the surface. The molecular area in this case depends not only on the natural dimensions of the molecules, but also, fundamentally, on the concentration of adsorption centers on the surface, and on their topography. It is necessary to take the latter into account, in the determination of the specific surface from the adsorption isotherms of substances which are specific to the chemical character of the adsorbent surface. The physical reality of the magnitudes presented in Table 4 for the molecular areas is determined by two circumstances: the first of these is the actual correspondence of the values of the constant a_m calculated from the BET adsorption isotherm for the capacity of complete unimolecular layers for the substances investigated; the second is associated with the physical reality of the specific surfaces of the adsorbents, especially with the chemical nonuniformity of the surface, when these are determined from the low temperature adsorption of nitrogen. Both these circumstances are bound up with the question of the applicability of the BET polymolecular adsorption theory to the systems here considered. In one of the subsequent communications in this series we shall give a detailed analysis and consideration of these questions.

For a formal determination of the capacity of the monolayer a_m we do not take into account the nonuniformity of the surface on the molecular scale. It is not necessary to accept the point of view of Kurbatov that "the BET theory gives, for the adsorption of water and other substances which able to participate in hydrogen bonds, not the whole surface, but the number of active centers" [32]; that is, in our case, the silanol portion of the sur-

face. Appropriate choice of the molecular areas will give magnitudes for this in individual cases which are in agreement with the surface calculated, for example, from the adsorption isotherm of nitrogen. If we now relate the experimental magnitudes for the adsorption of water to the size of surface calculated from the same isotherms, then the absolute isotherms obtained will approximate to each other and will coincide, since, in the calculation of the specific surface, the qualitative difference in the latter is automatically taken into account in its size. If we suppose, in agreement with [22], that the molecular area of water is 26 A, then, if the magnitudes of the adsorption given in Fig. 1 are divided by the specific surface determined from these isotherms, the absolute adsorption isotherms obtained are close to one another (Fig. 5). The difference which does exist is apparently connected with nonuniformity of the topography of the hydroxyl groups on the surface of these silica-gels. The broken line on the graph denotes the absolute adsorption isotherm of water vapor on hydrated coarse-pored silica-gels, taken from [24].

CONCLUSIONS

1. Substitution of a portion of the hydroxyl groups of the surface of silica-gel by methyl groups leads to a reduction of its adsorption power for substances in the vapor state, and to a considerable increase of the molecular area for complete unimolecular layers.

2. The determination of the specific surface of adsorbents with chemically nonuniform surface, based upon the application of the BET adsorption isotherm equation, requires careful attention to the choice of those substances for adsorption which are least sensitive to the chemical nonuniformity of the surface.

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THE COMPOSITION OF THE ACIDS FORMED BY THE OXIDATION
OF n-DECANE IN THE LIQUID PHASE

L. K. Obukhova and N. M. Émanuel'

Institue of Chemical Physics of the Academy of Sciences of USSR
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Among the problems connected with the practical exploitation of the oxidative transformation of hydro-carbons, the question of the composition of the mixture of acid products formed is of great importance. Thus, for example, the region of application of the synthetic fatty acids produced by the oxidation of the paraffins is in direct dependence on the nature of the distribution of the acids according to molecular weight, and this itself is determined by the conditions under which the oxidation is carried out. A knowledge of the detailed composition of the oxidation products is also necessary if one is to determine the mechanism of the oxidation, which plays a decisive role for the development of existing technological processes and the creation of new ones.

This question is touched upon to a greater or less degree in all works on the oxidation of paraffins and on mixtures of paraffins of various molecular weights, but the rather poor accuracy of the methods of analysis which have been used, has led to the fact that there is at the present time no united opinion on the mechanism of the oxidation process which leads to the production of fatty acid molecules from hydrocarbon molecules. It is usual only to give general data on the composition of the acid fraction produced by the preparative process. Most often this information is obtained by rectification of the mixture, either of the raw fatty acids themselves, or after preliminary esterification of the mixture. Practically no information is available on the kinetic behavior of the acids in the course of the reaction, which makes it very difficult to solve the question as to the nature and the scale of the change in the composition of the acid mixture with increase in the extent of the transformation.

The present work is devoted to the problem of investigating the qualitative composition of the acid mixture and of revealing the quantitative kinetic regularities of the behavior of individual acids in the course of the reaction. For this purpose it was necessary to obtain more detailed data on the mechanism of liquid phase oxidation.

EXPERIMENTAL

The raw material for the investigation was synthetic n-decane. The apparatus, the experimental conditions and the method of determining the reaction products (peroxides, carbonyl compounds, alcohols, acids and saponifi-able products) are those described in a previous publication [1]. The oxidation was performed, without the use of a catalyst, in a stream of oxygen at a temperature of 140°.

A special method was worked out for separating the fractions of the free acids, and for their analysis with respect to the individual components [2,3]. The free acids were obtained by a double distillation in steam, the first time after the precipitation of the acids by sodium bicarbonate, and the second time from an acid medium. Their total composition in the sample was determined by a preliminary titration with 0.1 normal alcoholic sodium hydroxide. The acids were then brought quantitatively into benzene solution, and then methylated by means of diazomethane. The solution of the methyl esters of the acids was used to obtain the hydroxamic deriva-tives, and subsequent identification of these was performed by means of paper chromatography.
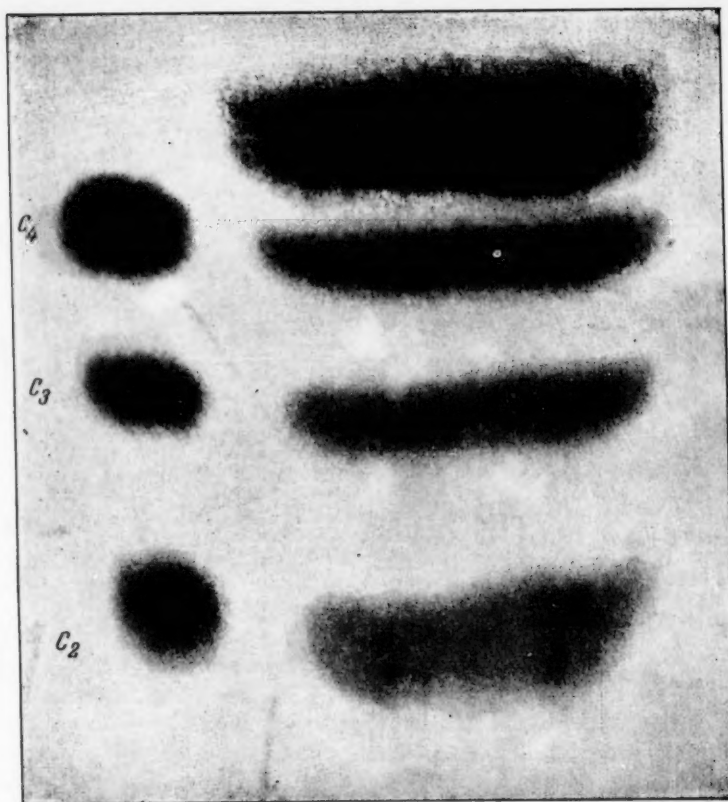
Fig. 1. Chromatographic separation of a mixture of lower fatty acids: left hand side: standard mixture of acids in the range C_2-C_4; right hand side: mixture of the lower acids from an experiment involving 4.5 hours' oxidation.

For the separation of the mixture of acids from formic to butyric the system used was: n-butanol-water-acetic acid (40 ml: 50 ml: 3.5 ml); for the separation of the mixture of acids from C_5 and above, up to C_{10}, the system used was: benzene-water-formic acid (1:1:1). For the identification and the quantitative determination of the components of the acid mixtures, it was sufficient to use amounts of the oxidate contained in a mixture of total acidity $10-15 \times 10^{-4}$ M. Every stage of the analysis was rigidly standardized, and it was therefore possible to obtain reproducible results. A further criterion of the accuracy of the work was provided by the total of the acid amounts found, which led to an estimate of the precision of 5-8%. The clarity of the resolution of the standard acid mixture and the mixture of acids arising in the course of the oxidation of n-decane, can be seen by the photograms of the chromatographic determinations reproduced in Figs. 1 and 2. For the quantitative determination of the acid content, the iron-hydroxamic complexes were transferred to paper in a solution of ferric perchlorate, the optical density of which was measured at 510 mμ on a spectrometer of type SF-4.

Since the mixture contained not only monocarboxylic acids but also hydroxy- and keto-acids, a special method was worked out for determining these. The usual methods for determining hydroxy-acids (from the solubility of the acid mixture in petroleum ether) could not be regarded as sufficient, since they presuppose operations with large quantitites of the substance. For the determination of hydroxy-acids in a mixture containing monocarboxylic acids we used the following method. The dry residue of the mixture of sodium salts of the acids was acetylated in a hermetically sealed vessel by means of acetyl chloride, for a period of $1\frac{1}{2}$ hours. After the excess of acetyl chloride had been dissolved in water (2 ml) the acetyl derivative formed was extracted by means of 20 ml of diethyl ether, which had previously been purified by boiling with 20% aqueous sodium hydroxide. The ethereal extract was treated further by a solution of hydroxylamine in methanol. After being allowed to stand for an hour at room temperature, the quantity of the acetylhydroxamic acid obtained was determined colorimetrically from its reaction with ferric perchlorate. Calibration was carried out by using α-hydroxyisocaproic
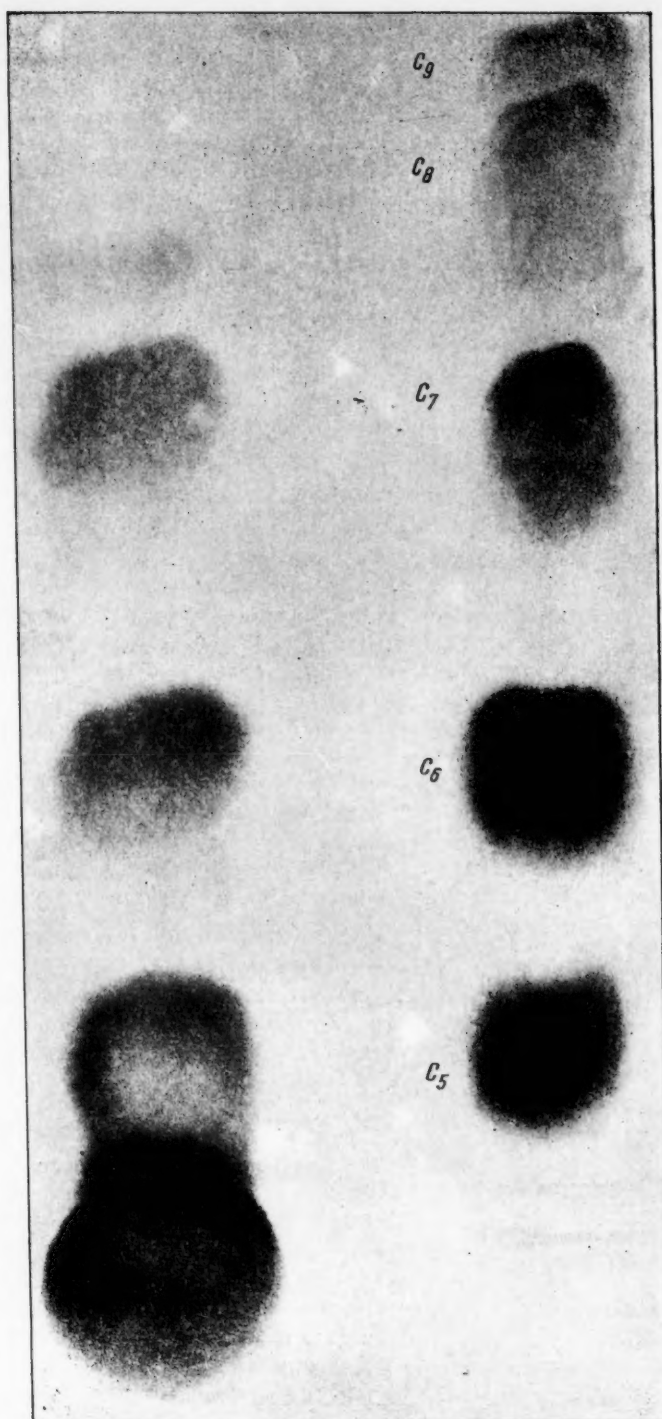
Fig. 2. Chromatographic separation of a mixture of higher fatty acids: right hand side: standard mixture of acids in the range C_5-C_9; left hand side: mixture of acids from an experiment after 4.5 hours' oxidation.
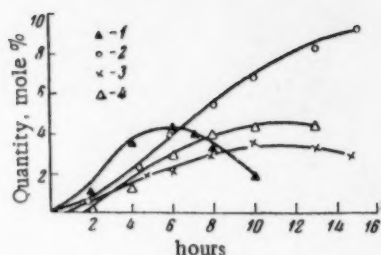
Fig. 3. Kinetic curves for the production of the basic products of oxidation:
1) peroxides; 2) acids; 3) alcohols; 4) carbonyl compounds.

acid. The limit of sensitivity of the method was 0.5×10^{-5}M of the hydroxy acid in the sample. The determination of the ketonic acids was carried out by their reaction with 2,4-dinitrophenylhydrazine in hydrochloric acid solution. The reaction is very sensitive, and it is possible to detect qualitatively the presence of ketonic acids when the concentration in the sample is as little as 1×10^{-7}M. The standard solution for this determination was pyruvic acid. Fig. 3 gives the

Fig. 3 gives the kinetic curves for the development of the basic products of oxidation: peroxides, carbonyl compounds, alcohols and acids; these curves give an impression of the general course of the reaction. It is characteristic of the reactions, that the products of the more intense oxidation, i.e. ketones, alcohols and acids, are formed in appreciable quantities from the very start of the reactions, with comparable velocities. The retardation of the formation of alcohols and kentones begins somewhat earlier than that of acids. All the kinetic curves for all the three products are of similar types. An exception to this is the kinetic curve for the formation of hydroperoxides, which have a clear maximum. This is quite natural, since the hydroperoxides arise as intermediate oxidation products.

The following qualitative conclusions may be drawn from an examination of the chromatograms, as to the basis of the acid composition. It is important to note that the mixture of acids does not include an acid of the C_{10} chain, that is, of the same chain length as the initial hydrocarbon, the formation of which in the course of the reaction is theoretically completely possible. In addition to this, the high molecular weight acids containing C_9 and C_8, and also formic acid, are present only in traces. Thus the acid products consist essentially of mixtures of low molecular weight acids and acids of intermediate molecular weight. The kinetic curves for the formation of the individual acids (Fig. 4) were obtained in the following fashion. At predetermined stages of the process a sample of the oxidate was removed and was analyzed in the way described above for the content of individual acids in the mixture. Analysis of the kinetic behavior during the reaction of the individual acids led to the following conclusion: the kinetic character of the curves is not changed with increase in the extent of conversion, and does not depend on the molecular weight of the acid. Attention is directed to the fact that the acids from acetic to valeric are formed practically in the same quantities, while the extent of the production of caproic acid (C_6) is somewhat less, and the acid containing C_7 is formed in quantities approximately factor of 2 less than all the other acids. The relative quantites of the acids, however, remain practically constant throughout the whole of the investigated time interval.
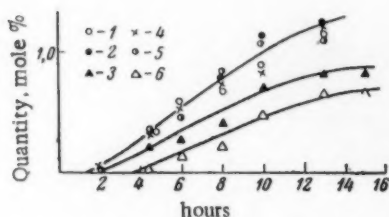
Fig. 4. Kinetic curves for the development of the individual acids: 1) acetic; 2) butyric; 3) caproic; 4) propionic; 5) valeric; 6) enanthic.

In connection with the functional composition of the mixture of acids from the analysis data given in Table 1, it appears that the ratio between the ketoacids, hydroxyacids and monocarboxylic acids remains constant in the course of the process. The quantity of hydroxy- and ketoacids does not exceed 18% of the total acids formed in the course of the oxidation.

DISCUSSION OF THE EXPERIMENTAL RESULTS

The composition of the acid mixture produced by the oxidation of hydrocarbons may in principle depend not only on the mechanism of those stages which produce the acid molecules, but also on secondary processes of oxidation, by which the acids themselves produced in the course of a reaction, may be affected. It is known that the capacity for oxidation of the fatty acids increases very greatly with increase in the molecular weight of the acids. Zerner [4] in an investigation of the oxidation of stearic acid discovered that it is oxidised rather readily at 115° in the presence of a catalyst, giving predominantly low molecular weight acids. Under the same conditions the acids of lower molecular weight (C_{12} and C_{14}) give rise practically to no detectable oxidation products, while the acids containing C_8 are not changed at all. Mannes [5] drew similar conclusions from a comparison of the capacity for oxidation of the soap-forming acids ($C_{12}-C_{18}$) and the "pre-distilled" acids (C_6-C_9).

In our case the conditions of oxidation were more vigorous (140°), which may have facilitated the oxidative destruction of the acids. So as to find out whether under the conditions of our experiments the second process of

TABLE 1

Composition of acid mixture obtained by the oxidation of n-decane at 140°

Time of reaction in hours	Total acids, mole %	Composition in mole %			Quantity of mono-carobxylic acids as % of total acids
		keto-acids	hydroxy-acids	monocar-boxylic acids	
4,5	2,40	0,08	0,36	1,96	82
6	4,20	0,20	0,56	3,44	82
8	5,60	0,30	0,60	4,70	84
10	6,92	0,20	0,74	5,98	85
13	8,20	0,36	0,58	7,26	88
15	9,40	0,42	0,85	8,13	86

oxidation of the acids took place, we have carried out the following experiment. At the first moment of the reaction there was introduced a large excess (1.6 mole %) of caprylic acid, an acid which itself is formed only in negligibly small quantities in the course of oxidation. We then traced the behavior of this added acid during the course of oxidation. By analyzing the acid fraction after 2.5 and 10 hours of oxidation, we were able to establish that there was no appreciable reduction in the quantity of the added acid (Table 2).

TABLE 2

The caprylic acid content of the acid mixture

Time of oxidation in hours	0	2	5	10
Content of C_8 acid in moles %	1,60	1,56	1,72	1,60

Thus, although the added acid existed for a period of 10 hours in a zone where the oxidative destruction was actively proceeding, it was not involved in the reaction. Further analysis of the mixture of acids obtained in this reaction gave no evidence of any deviation in the composition of the mixture from that which was obtained by the oxidation of pure n-decane. It was necessary to conclude, therefore, on the basis of these facts, that the distribution of the individual components of the acid mixture which was found in the oxidation of the C_{10} hydrocarbon, was uncomplicated by any combustion of the acids formed. At first glance this confirmation is contradicted by the presence in the mixture of a certain quantity, however small it may be, of hydroxy- and keto-acids, the production of which by the secondary oxidation of the fatty acids seems to be most likely. It is possible that this assumption may prove to be correct for the case of high molecular weight acids, but under the conditions of our experiments it is completely excluded. The following conlcusions may be drawn in relation to the structure and the molecular weight of those hydroxy-acids which are present in the analyzed mixture. The acids in question are, without exception, α-hydroxy acids (which are volatile in water vapor, and do not give lactones), and therefore in all probability consist of a mixture of the C_3 and C_4 hydroxy-acids. Freshly obtained chromatograms show, intervening between acetic and propionic acids and between propionic and butyric acids, traces of certain acids which are very rapidly lost, and cannot in fact be seen upon the photographs. It may well be that these acids consist of hydroxypropionic and hydroxybutyric acids. It would appear that the presence of hydroxyl groups in the molecules of these acids reduces the value of R_f, in comparison with the values corresponding to the fatty acids in the system of solvents which we have employed for the development of our chromatograms [6]. The question of the manner in which the hydroxy- and keto-acids arise during the oxidation of n-decane will be given special consideration later and will not be discussed further here.

In a group of papers [7, 8] on the oxidation of hydrocarbons of intermediate molecular weight—n-heptane, n-decane and n-dodecane—it has been shown that the peroxidic and carbonyl compounds and alcohols, which are produced for small degrees of conversion of the hydrocarbons, occur in the form of an equimolecular mixture of all the theoretically possible secondary hydroperoxides, secondary alcohols and ketones which preserve the hydrocarbon skeleton of the initial hydrocarbon. The conclusion to be drawn on the basis of these facts is, that the primary introduction of the oxygen into the hydrocarbon molecule proceeds with equal probability at all the secondary C—H links. The most usually accepted assumption about the mechanism of the formation of acids by the oxidation of hydrocarbons in the liquid phase appears, at the present time, to be the production of α-peroxidic ketones, according to the following scheme:

$$RCH_2C(\!=\!O)\!-\!CH_2CH_2R_1 \xrightarrow{O_2} RCH_2C(\!=\!O)\!-\!\underset{OOH}{CH}\!-\!CH_2R_1 \rightarrow$$

$$\rightarrow RCH_2C\!\!\begin{array}{c}O\\OH\end{array} + \begin{array}{c}O\\H\end{array}\!\!C\!-\!CH_2R_1 \xrightarrow{O_2} R_1CH_2C\!\!\begin{array}{c}O\\H\end{array}$$
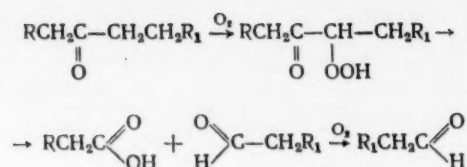
followed by the formation of two acid molecules from the ketone molecule. This has been shown quite clearly for the case of the cyclic ketones (cyclohexanone, tetralon) [9].

The results obtained by us are not, however, in harmony with this point of view. If the oxidation of decanones (the presence of which in the mixture of reaction products may be regarded as demonstrated) was in fact only accomplished on those atoms occurring in α-positions relative to the carbonyl group, then we ought to obtain equal molecular quantities of acids, for example, acetic and caprylic (C_2 and C_8), propionic and enanthic (C_3 and C_7) etc. What we have found, however, is a predominant amount of the lower molecular acids in the mixture. Such a picture cannot be explained by secondary oxidation of the acids, since under the conditions which we have used, it has been shown above, that these do not occur. In order to provide a detailed solution of the problem of the mechanism whereby acids arise during the oxidation of liquid paraffins, it seems to us necessary to carry out more detailed investigations of the oxidative conversion of the precursors—ketones and alcohols—using as starting point sufficiently high molecular weight compounds possessing linear hydrocarbon radicals.

CONCLUSIONS

1. The composition of the mixture of acids, and the kinetics of the behavior of the individual acids, have been studied for the oxidation of n-decane in the liquid phase.

2. It has been shown that oxidative combustion of the higher acids during the oxidation process does not occur.

3. The distribution of the acids obtained cannot be explained on the basis of the suppositions accepted at the present time, and needs a more thorough investigation of the mechanism of the separate stages taking place during the complex oxidation process leading to the development of the acids.

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THE DIPOLE MOMENTS OF ORGANOLITHIUM COMPOUNDS
OF THE ALIPHATIC SERIES

V. N. Vasil'eva, V. V. Talalaeva, E. N. Gur'yanova
and K. A. Kocheshkov

The L. Ya. Karpov Physico-Chemical Institute

The organic compounds of lithium have acquired a great significance for synthetic organic chemistry. They have a wide application in the synthesis of numerous classes of organic and metallo-organic compounds. In recent times both the organolithium compounds themselves, and the products of their interaction with other metallic compounds, such as titanium tetrachloride, have found application as catalysts for polymerization processes. This fact has led to increased interest in such types of compounds, some introduction to the structure of which may be obtained by a study of the polar properties of their components. Some information exists at the present time on the polarity of the carbon-lithium bond, but these are very scanty and contradictory. It is therefore of direct interest from this point of view that measurements should be carried out on the dipole moments of organo-lithium compounds, together with the determination of the polarity of the C-Li bond.

The dipole moments of ethyl- and butyllithium have been measured earlier [1, 2] in benzene solution. The authors themselves observe that the values of 0.86 D for ethyllithium and 0.97 D for butyllithium do not relate to the monomeric molecules, but to the associated molecules. This is fully in agreement with the published cryoscopic [3,4] and spectroscopic [5,6] data on the association of these compounds in benzene.

It is known from spectroscopic data [5,6] that organolithium compounds are considerably less associated in hexane than they are in benzene. Because of this, we have measured the dipole moments of ethyllithium, n-propyllithium, n-amyllithium and n-dodecyllithium in hexane, the measurements being carried out at the smallest practicable concentrations, since the probability of association is small under such conditions, and since we could determine the degree of association by cryoscopic measurements for these concentration values.

All these compounds were very unstable, and therefore their synthesis, the preparation of their solutions, and the measurements of their dipole moments were carried out in an atmosphere of pure argon. The solutions of all the organolithium compounds were obtained in the same way. A liter flask was provided with a dropping funnel, a stirrer, a reflux condenser (combined with a 3-way tap with an inlet tube for the current of argon), a thermometer, a syphon, and a side-tube equipped with a tap. Into this flask were introduced 500 ml of dry n-hexane, and lithium was introduced in an amount 2.5 g in excess of that required by calculation, the lithium having been finely shredded in an atmosphere of argon. The solution was brought rapidly to boiling point, and there was then added, during a period of 3-4 hours, drop by drop with constant stirring, 0.3-0.5 M of the alkyl-chloride diluted to 50-100 ml with n-hexane. There was then added a further 1-2 g of lithium, and the solution was boiled with stirring for a further 4-5 hours. The yield of the lithium alkyl was 87-95% of the theoretical figure. The solution obtained was siphoned off in an atmosphere of argon and filtered into a graduated vessel. The clear solution of the organolithium compound was either collected by means of pipettes filled with argon, or siphons in an atmosphere of argon into measuring vessels with hexane. The initial solution (25, 50, 100 ml)

TABLE 1

c	ε	d	c	ε	d
Measurement in hexane at 25°					
Ethyllithium			n-Amyllithium		
	1,8783	0,6618	0	1,8765	0,6618
0,12	1,8794	0,6618	0,13	1,8765	0,6633
0,19	1,8799	0,6618	0,28	1,8794	0,6650
0,27	1,8812	0,6619	0,42	1,8806	0,6665
0,37	1,8820	0,6619	0,52	1,8819	0,6677
0,62	1,8846	0,6621	0,66	1,8838	—
n-Butyllithium					
0	1,8790	0,66210	0,29	1,8816	
0,13	1,8810	—	0,36	1,8822	0,6624
0,26	1,8820	0,6623			
Measurement in benzene at 25°					
Ethyllithium					
0	2,2714	0,8698	0,30	2,2747	—
0,094	2,2727	—	0,49	2,2772	0,8703
0,20	2,2743	0,8700			

was poured into the quantity of hexane necessary to bring the total volume of the solution up to a definite value (150-200 ml). The solution obtained was carefully mixed and, by means of a pipette filled with argon, was introduced in the necessary amount into an ampoule filled with argon.

The concentration of the solution was determined by titration. For this purpose a sample from the solution, of 10-25 ml in volume, was poured into n-hexane diluted by alcohol, water was added, and the mixture was titrated with vigorous stirring by 0.1 N sulfuric acid. The solution of ethyllithium in hexane or in benzene was prepared from a weighed quantity of pure ethyllithium. The ethyllithium was produced in an atmosphere of nitrogen from ethyl chloride and lithium in "cryoscopic" benzene, and was separated in a crystalline form and recrystallized from hexane.

The dipole moments were measured in hexane solutions at 25° by the beat-method. The results of measurements in the concentration range from 0.094-0.66 mole % are shown in Tables 1 and 2. The results in the concentration range 0.6-7.5 mole % are shown in Table 3. The following symbolism is used in the table: c = concentration of the dissolved substance in moles %; ϵ = dielectric constant of the solution; d = density of the solution; P_∞ = molecular polarization of the substance at infinite dilution. Extrapolation of the molecular polarization to infinite dilution was carried out by the Khedestrand method; P_E = electronic polarization of the substance, regarded as being the same as the molecular refraction for the D-line of sodium, and calculated on an additive basis. The refraction of lithium was taken as 1.17 cm³. The dipole moment μ was calculated from the formula:

$$\mu = 0,0127 \cdot 10^{-18} \sqrt{(P_\infty - P_E)\, T}.$$

It can seen from Table 1 that the relationship between the dielectric constant of the solution and the concentration is rectilinear within the concentration ranges: 0.12-0.62 mole % for ethyllithium, 0.13-0.36 mole % for butyllithium; 0.13-0.66 mole % for amyllithium. The dipole moment calculated from the experimental data, μ, for all the three cases was 1.1 D. From the rectilinear relationship between the dielectric constant of the solution and the concentration, and also from the constancy of the value of the dipole moment for the three compounds, it follows that within the given concentration range we are concerned with monomeric molecules, and the value of 1.1 D for the dipole moment of ethyl- butyl- and amyllithium is that of the monomer. In measuring the dielectric constant of solutions of alkyllithium compounds in hexane for higher concentrations (Table 3), deviation from the straight line relationship was observed, most clearly expressed for solutions of ethyllithium in the concentration range 0.62-3.27 mole %.

It seems that the deviation from the straight line relationship, and the reduction of the dipole moment of ethyllithium with increase in the concentration, is due to the association of the molecules with the formation of

TABLE 2

Compound	Solvent	Concentration, mole %	P_∞	P_E	$\mu \cdot 10^{18}$
Ethyllithium	hexane	0,12 —0,62	36,4	11,5	1,1
	benzene	0,094—0,49	26,9	11,5	(0,87)
n-butyllithium	hexane	0,13 —0,36	44,4	20,7	1,1
n-amyllithium	hexane	0,13 —0,66	48,8	25,4	1,1
n-dodecyllithium	hexane	1,0 —5,7	77,7	57,6	(0,99)

TABLE 3

c	ε	d	c	ε	d
Ethyllithium			n-Amyllithium		
0	1,8784	0,6618	0	1,8820	0,6618
0,62	1,8821	0,6621	1,63	1,8930	0,6636
1,78	1,8892	0,6627	3,23	1,9063	0,6655
2,55	1,8924	0,6631	4,45	1,9098	0,6670
3,27	1,8951	0,6636	6,04	1,9239	0,6688
3,63	1,8950	—	7,53	1,9363	0,6705
n-Propyllithium			n-Dodecyllithium		
0	1,8797	0,6637	0	1,8790	0,6642
1,28	1,8874	0,6644	1,01	1,8870	0,6650
2,68	1,8942	0,6652	1,99	1,8953	0,6685
3,90	1,9014	0 6659	2,89	1,9091	0,6715
5,06	1,9078	0,6664	3,91	1,9189	0,6728
6,44	1,9163	0,6674	4,85	1,9293	0,6759
			5,71	1,9391	0,6788
n-Butyllithium					
0	1,8767	0,6623	2,89	1,8921	0,6642
0 78	1,8803	0,6626	4,77	1,9044	0,6656
1 43	1,8860	0,6635	6,85	1,9157	0 6674

complexes; this is in good agreement with the cryoscopic data [3,4], and with the infra-red spectroscopic data [5]. Increase in the length of the chain of the aliphatic radical from ethyl to amyl, as we would expect, causes the degree of association of the lithium alkyls to diminish. Thus, in solutions of propyl- butyl- and amyllithium, interaction occurs at concentrations higher than 2 mole %, while the apparent value of the dipole moment of dodecyllithium, 0.99 D is very close to the value of the dipole moment of the monomeric molecules. The effect of the extension of the length of the aliphatic radicals on the behavior of the lithium alkyls in solution will be considered in further investigations by ourselves.

Thus, measurements of the relationship between the dielectric constant and the concentration of lithium alkyls in hexane has made it possible to calculate the dipole moment of the monomeric molecules at low concentrations, while association is observed at concentrations between 0.6 and 6.0 mole %. It has also permitted us to state that the degree of association of the molecules depends on the structure of the aliphatic radical.

The behavior of the lithium alkyls in benzene solution is different from their behavior in hexane. As we have shown above, Rogers and Brown [2] attribute the value of the dipole moment obtained by themselves, 0.86 D for ethyllithium in benzene within the concentration range 2-6 mole %, not to the monomeric molecule, but to the associated molecule. Since, however, an equilibrium exists between the monomeric molecules and the associated molecules, the dielectric constant of the solution will not be a linear function of the concentration, as these authors observed. We have measured the dipole moment of ethyllithium in benzene at 25° in the concentration range 0.094-0.49 mole % and have obtained a value of the apparent moment 0.87 D, close to the value obtained by Rogers and Brown. It appears that ethyllithium in benzene solution forms stable complexes, even at quite low concentrations. Infra-red spectroscopic data [5] show that the relative quantity of monomeric molecules of ethyllithium in benzene is small, even in very dilute solutions.

CONCLUSIONS

1. The dipole moment of ethyl-, n-butyl-, and n-amyllithium have been measured in hexane. The value found for $\mu = 1.1$ D.

2. Lithium alkyls are associated both in hexane and in benzene solutions.

3. The degree and the nature of the dissociation depends on the structure of the aliphatic radical, and on the nature of the solvent.

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THE EFFECT OF THE NATURE OF THE SUBSTITUENTS
ON THE SILICON ATOM ON THE FREQUENCY OF THE FULLY
SYMMETRICAL VALENCE VIBRATION OF Si−C IN THE SPECTRA
OF ORGANOSILICON COMPOUNDS.

Yu. P. Egorov

The N. D. Zelinksii Institute of Organic Chemistry, Academy of Sciences of USSR

Investigation of the Raman spectra of various classes of silico-organic compounds has led us to the conclusion [1-3] that alkyl- and alkenyl-radicals when combined with the silicon atom have no significant mutual interaction. The silicon atom plays the part of a barrier which prevents their interaction. This fact is revealed, for example, in the high specific oscillation frequencies, and intensities of the corresponding lines, associated with individual radicals or bonds [1-3]. It is apparently, because of these properties of the silicon atom that the frequency of fully symmetrical valence oscillation ν(Si-C) is insensitive to the mass of the radical, as experiment shows. Since the frequency ν(Si-C) is, in spite of this, different in various compounds, it is reasonable to expect that there should be a fundamental relationship between the nature of the radical P_i (that is, the state of the electronic orbitals of each of the Si-C bonds), and the frequency ν(Si-C). The present communication is devoted to an investigation of this relationship, which is a matter of considerable interest, since, on the one hand it makes it possible to give precise limits to the distribution of the frequencies ν(Si-C) (which in a number of cases are still in dispute [3]), and, on the other hand, it enables us to obtain quantitative characteristics for the intramolecular effect of various radicals R_i on the electronic orbitals of the silicon atoms.

Data are found in the literature on the existence of a relationship of this kind for certain classes of chemical compounds. Bell, Heisler and other workers [4] have considered the effect of substituents on the frequency of the

$$\overset{\displaystyle X}{\underset{\displaystyle Z}{\overset{\displaystyle |}{\underset{\displaystyle |}{Y-P}}}}=O$$

oscillation ν(P=O) in the tetrahedral molecule $Y-\overset{X}{\underset{Z}{P}}=O$, and have observed that this frequency is independent

of the mass of the substituents X, Y and Z, although it is a linear function of the sum of their electronegativity. The authors have discovered an empirical equation which makes it possible to predict the frequency ν(P=O) in various molecules. Starting from this formula, they have determined the so-called "group electronegativity" or "displacement constant" of the frequency ν(P=O) for many radicals. A similar type of relationship, this time for the frequency ν(C=O) in molecules of the type $\overset{X}{\underset{Y}{\diagdown}}C=O$ and the total electronegativity of X and Y, has been found by Kagarise [5]. Agreement with the experimental data in this work however, is considerably worse than that discovered by Bell [4]. Bellamy [6] has studied the influence of the inductive and mesomeric effects on the position of the oscillation frequencies, which are independent of the effect of mass. He has come to the

conclusion that, for the nonplanar tetrahedral molecule $Y-\overset{X}{\underset{Z}{P}}=O$ [4], the mesomeric effect is absent, and there-

fore the group electronegativity is in this case a measure of the pure inductive effect of the radicals. In the planar

molecules $\begin{array}{c} X \\ \diagdown \\ \diagup \\ Y \end{array} C = O$ [5], the mesomeric effect which can also take place complicates the picture, and the group

electronegativity discovered in work [5] is a measure of both the effects. Wilmshurst [7], in investigating the relationship between the deformation oscillations of the methyl and the silyl groups in the molecules CH_3-X and SiH_3-X and the nature of the halogen X, has observed that the square of the frequency of the symmetrical deformation oscillation in the CH_3 and the SiH_3 groups is a linear function of the electronegativity of the X atom. Since there can be no conjugation effect in such types of molecule, the author suggests the determination of the effective electronegativity of the radicals by starting from the experimental values of the frequencies of the deformation oscillations of the methyl group in molecules of the type CH_3-X. It is unfortunate that the series of electronegativities obtained by the author in this way contradicts the generally accepted order, since, for example, the amino- and hydroxyl-groups are found to be more electronegative than chloride and the nitro-group.

The literature does not at present reveal any agreement on the range of distribution of the frequencies ν(Si-C) [3]. Certain authors give the range as 600-700 cm^{-1} and above. For the simplest molecules such as $Si(CH_3)_4$ it has been convincingly established [8, 9] that the fully symmetrical oscillation ν(Si-C) has a frequency of 595 cm^{-1}. The frequency ν(Si-C) in the methylchlorosilanes [9-11] is also reliably established. In the more complicated organo-silicon compounds the derivation of the frequencies is either arrived at by analogy with more simple molecules, or is, to a considerable degree, provisional and uncertain. It should be noted that in [12-13] attention has been directed to the connection between the frequency ν(Si-C) and the nature of the substituents, although this relationship has not been studied.

Comparison of spectra of various compounds of the type $Si(R_1R_2R_3R_4)$, in which R_i represents an aliphatic group, from the data available in the literature and in the main obtained recently by ourselves, leads to the conclusion that the symmetrical frequency ν(Si-C) is distributed within the range 500-700 cm^{-1}. It is usually not difficult to identify this frequency in the spectrum, since it is intense and polarized. This line is particularly intense when the compound contains at least three simple radicals of a single type (Ch_3, C_2H_5). Since the line is several times more intense than other lines occurring in this region, it may be supposed that the form of the normal oscillation corresponding to the given frequency is associated with the maximum change of the ellipsoid of polari-

$$\begin{array}{c} C_{(1)} \\ | \\ C_{(3)}-Si-C_{(2)} \\ | \\ C_{(4)} \end{array}$$

zability of the framework, that is, the frequncy under consideration is pulsational. With such form of oscillation, change occurs simultaneously in all the Si-C bonds, and, consequently, the frequency of such an oscillation is determined by some total value of the quasi-elastic constants of the individual bonds. If one of the radicals is replaced by a radical of another structure, a redistribution of the electronic density occurs in the orbital of the Si atom, which in its turn affects the position of the frequency of the fully symmetrical oscillation. Experiment shows that the more electronegative radicals increase the frequency ν(Si-C), while the less electronegative ones reduce this value. Accumulation of similar radicals at the silicon atom leads to a shift of the frequency of the corresponding total effect.

This discussion of the data concerning the behavior of the frequency ν(Si-C) has made it possible for us to look for a relationship between the nature of the radicals and the magnitude of this frequency, using a method similar to that used in [4-7]. Returning to the simplest group of compounds, the methylchlorosilanes, $(Cl_{4-n})Si$ $(Ch_3)_n$, where n = 0, 1, 2, 3, 4; for which the values of ν(Si-C) have been reliably determined, while the electronegativity of the chlorine atom is generally accepted as equal to 3.0 (according to Pauling, both here and subsequently); we have obtained the graphical relationship which is shown in Fig. 1. This gives, in agreement with [4], a value of the effective electronegativity of the methyl group of 2.0. Following the practice of [4-7], we have used the term "effective electronegativity (eff. EN) of the radical", although, in our opinion, this is not entirely satisfactory for the description of the phenomena observed here. An examination of the publications on this question (see, for example, the review [14]) shows that the values of the electronegativity, even for such simple atoms as that of carbon, may vary from 2.5 to 2.63; while for other atoms the variation is even greater. No method has, apparently, yet been developed for the unique estimation of the magnitude of the electronegativity, which depends, as special investigations have shown, on the state of the electronic orbital of the atom under investigation,

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and on the nature of the bond between this atom and neighboring atoms, etc. It is therefore not difficult to appreciate how complicated this problem becomes, when it is concerned with the determination of the electronegativity of a radical; here there enters into the problem of the intramolecular interaction of the bonds, steric factors and other effects. For this reason we understand by the term "effective electronegativity" a quantitative expression of the total effect of the radical (or atom) on the electronic orbital of the silicon atom, affecting the change in the elastic constants of the Si-C bonds. The Si-C bond is believed to be $\sim$ 13% ionic [15].

In Fig. 1 the axis of abscissas represents the total effective negativity of the radicals combined with the silicon atom, while the axis of ordinates represents the frequencies ν(Si-C). The relationship shown on the figure is in good agreement with the equation:

$$\nu = \frac{1655}{\sqrt{15,77 - \Sigma e_i}}, \qquad (1)$$

where ν =frequency of fully symmetrical valence oscillation ν (Si-C) in cm^{-1}; Σe_i= total effective electronegativity of the four substituents on the silicon atom. It appears that equation (1) is valid not only for methylchlorosilanes, but also for other classes of organosilicon compounds, which are described in Tables 2 and 3 below. Knowing the effective electronegativity of certain substituents (Cl, CH_3), and determining the experimental values of the fully symmetrical frequencies ν (Si-C) for molecules with various combinations of radicals on the silicon atoms, we have calculated for these the values of the effective electronegativity (cf. Table 1).

Fig. 1. Graphical presentation of the relationship between the total effective electro-negativity of radicals and ν (Si -C).

Table 1 shows clearly the complex nature of the relationship between the structure of the radical and the magnitude of its effective electronegativity. While it is difficult to draw any precise conclusions as to the reason for the connection between the structure of the radical and its electronegativity, one conclusion is certainly possible: the values obtained for the effective electronegativity are basically in agreement with the order accepted in the literature [16]: $Cl > Br > C_6H_5 > OCH_3 > CH_3 > C_2H_5 > i\text{-}C_3H_7$, and the results of the work of Bell [4]. The greatest deviation from the accepted values has been obtained by us for the benzyl radical,

$\left(CH_2 - \left\langle \overline{\underline{\qquad}} \right\rangle \right)$ where we obtain 2.29 instead of the expected 1.2-1.3 [14]. This may possibly be explained by

the specific interaction existing between the Si-C bond, and the aromatic nucleus which is situated in the β -position to it [17]. There is some reduction in the value of the electronegativity also for vinyl (1.93 against $\sim$ 2.1). It can be taken that the experimentally determined frequency ν (Si-C), and the subsequent calculation on the basis of equation (1), may serve as a method for the quantitative determination of the magnitudes of the effective electronegativity of radicals, in the sense understood above, for the molecules or organo-silicon compounds.

It is interesting to note the low value of the electronegativity of those radicals whose presence in the molecules [2,3,17] causes a specific derangement of the Si-C bond, through interaction with the multiple bond or with the CH_3 group. Thus the effective electronegativity of the allyl-radical is equal to 0.88, while those of the vinyl and n-butenyl radicals are 1.93 and 1.85 respectively; the effective electronegativity of the ethyl group is equal to 1.67, while that of the methyl and n-propyl radicals is equal to 2.0. The last fact is of particular interest, since it is believed that the energy of the Si-C bond is continuously decreased [18] from the methyl to the n-propyl radicals and beyond. In the isopropyl radical the effect of the methyl group is revealed in an even greater degree, and its effective electronegativity amounts to 1.34.

Tables 2 and 3 give the values of the fully symmetrical frequencies ν (Si-C), determined from the Raman spectra of $\sim$ 70 organosilicon molecules. These molecules contain various radicals in various mutual combinations. This variety has made it possible, as has been indicated above, to calculate the effective electronegativity of radicals, and simultaneously to confirm the applicability of equation (1). In consecutive columns of the Table are shown: references to the literature from which the Raman spectra have been obtained (if no reference is given the data are our own); the total effective electronegativity of the four radicals (Σe_i); the experimental values of

TABLE 1

Effective Electronegativity of Radicals

Radical	Eff. EN	Radical	Eff. EN
Cl	3,0	$CH_2CH(CH_3)CH_2CH=CH_2$	2,2
Br	2,85	$CH_2C(CH_3)=CH_2$	2,06
$-CH=CH-CH=CH_2$	2,65	$Si\begin{cases} CH_2-CH_2 \\ CH_2-CH_2 \end{cases}$	4,12
$-C_6H_5$	2,58		
$CH=C(CH_3)_2$	2,53	CH_3	2,0
$CH_2CH_2C_6H_5$	2,53	$n\text{-}C_3H_7$	2,0
$CH=CH-CH_3$	2,53	$n\text{-}C_4H_9$	2,0
$CH_2-CH=C=CH_2$	2,46	$CH_2CH_2C\equiv CH-$	1,93
$-CH_2-C_6H_5$	2,29	$-CH=CH_2$	1,93
		$CH_2CH_2CH=CH_2$	1,85
		$-CH_2CH_3$	1,67
		$CH(CH_3)_2$ *	1,34
		$-CH_2CH=CH_2$	0,88

* The effective electronegativity is here determined from the spectrum of
only 1 molecule containing the given radical.

of the frequency ν (Si-C) (ν_e); values calculated from equation (1) (ν_B); and the difference in these values $\Delta = \nu_B - \nu_e$. The experimental values ν_e, used as starting values in the calculation of the effective electronegativity of the radicals, are denoted by an asterisk; the corresponding radicals are also denoted by an asterisk.

As we can see from Table 2, the value of $\Delta = \nu_B - \nu_e$ B, in the majority of cases is small; and lies within the limits of experimental error, or of the conditions in which the spectra were obtained. From this we may draw the conclusion that equation (1) is valid for molecules containing the various radicals in any combination one with another. Consequently the magnitude ν (Si-C) in the final calculation is determined by the values found for the effective electronegativity of the individual substituents, while the factors for the interaction of the Si-C bonds for the compounds shown in Table 2 play a subordinate role. Starting from this point, it may be supposed, that for molecules in which considerable interaction occurs between the Si-C bonds, the experimental values for the fully symmetrical frequency ν (Si-C) will deviate from those calculated according to equation (1). This is also observed for the alkylsilanes, for which the data are given in Table 3.

If we follow the usual procedure for the determination of the effective electronegativity of the radical, and, starting from the values of ν (Si-C) for $(CH_3)_3Si-CH_2CH=CH_2-$as 555 cm^{-1}, calculate the electronegativity of the allyl radical, then the value obtained is 0,88. If we use this value for the calculation of ν (Si-C) for molecules containing one allyl group, satisfactory results are obtained. However, attempts to calculate the value of ν (Si-C) by this means for molecules containing several allyl groups, lead to a great reduction in the value of the results. This difficulty can only be overcome by introducing into equation (1) the empirical correction term, found by taking into account the interaction of the allyl groups: $(\Sigma e_i) = \Sigma e_i + (n-1)$ 0,77, where n is the number of allyl groups. Equation (1) takes the form:

$$\nu = \frac{1655}{\sqrt{15,77 - [\Sigma e_i + 0,77\,(n-1)]}} \qquad (2)$$

Calculations have been performed on the basis of this equation, the results of which are given in Table 3. The rather larger divergence between the values of ν_e and ν_B for the molecule $(C_2H_5)_3SiCH_2CH=CH_2$ (16 cm^{-1}) may perhaps be explained by interaction of an additional kind, taking into account the specific groups ethyl and allyl referred to above.

TABLE 2

Frequencies ν (Si-C), Obtained Experimentally and Calculated

Compound	Literature reference	Σe_i	ν_e	ν_B	Δ
$(CH_3)SiCl_3$	[10]	11	759*	—	—
$(CH_3)_2SiCl_2$	[10]	10	690*	—	—
$(CH_3)_3SiCl$	[10]	9	636	636	0
$(CH_3)_4Si$	[10]	8	595	594	—1
$(C_2H_5)_4Si$	[19]	6,68	553*	549	—4
$(CH_3)Si(C_2H_5)_3$ *	[19]	7,01	559*	559	0
$(CH_3)_2Si(C_2H_5)_2$	[19]	7,34	568	570	2
$(CH_3)_3SiC_2H_5$	[19]	7,67	580	582	+2
$Si(CH=CH_2)_4$ *		7,72	584*	—	—
$(CH_3)_3SiCH=CH_2$		7,93	588	591	+3
$(C_2H_5)_3SiCH=CH_2$		6,94	556	557	—1
$(CH_3)_3SiC_6H_5$ *		8,58	617*	—	—
$(C_2H_5)_3SiC_6H_5$		7,59	580	579	—1
$(CH_3)_2C_6H_5(SiCl)$		9,58	660	665	+5
$(CH_3)_2Si(C_2H_5)(C_6H_5)$		8,25	605	604	—1
$(n-C_3H_7)_4Si$	[20]	8,0	591	594	+3
$(CH_3)_3Si(n-C_3H_7)$		8,0	602	594	—8
$(n-C_3H_7)_3SiCH=CH_2$		7,93	590	591	+1
$(n-C_4H_9)_4Si$	[20]	8	594	594	0
$(n-C_4H_9)Si(C_2H_5)_3$		7,01	568	559	—9
$(n-C_4H_9)_3SiCH=CH_2$		7,93	588	591	+3
$(CH_3)_3SiCH_2CH_2CH=CH_2$ *		7,85	588*	—	—
$(CH_3)_2(C_2H_5)SiCH_2CH_2CH=CH_2$		7,52	579	576	—3
$(C_2H_5)_3SiCH_2CH_2CH=CH_2$		6,86	556	555	—1
$(CH_3)_3SiCH=C(CH_3)_2$ *		8,53	615*	—	—
$(CH_3)_2Si[CH=C(CH_3)_2]_2$		9,06	650	639	—11
$(CH_3)_2(C_2H_5)Si-CH=C(CH_3)_2$		8,20	602	602.	0
$(CH_3)_2Si\begin{smallmatrix}CH_2-CH_2\\ \mid \\ CH_2-CH_2\end{smallmatrix}$		8,12	598	598	0
$(C_2H_5)_2Si\begin{smallmatrix}CH_2-CH_2\\ \mid \\ CH_2-CH_2\end{smallmatrix}$		7,46	582	574	—8
$\begin{smallmatrix}H_2C-H_2C\\ H_2C-H_2C\end{smallmatrix}Si\begin{smallmatrix}CH_2-CH_2 *\\ \mid \\ CH_2-CH_2\end{smallmatrix}$		8,24	603*	603	0
$(n-C_4H_9)_2Si\begin{smallmatrix}CH_2-CH_2\\ \mid \\ CH_2-CH_2\end{smallmatrix}$		8,12	601	598	—3
$(CH_3)_3SiCH_2CH(CH_3)CH_2CH=CH_2$ *		8,20	602*	—	—
$(C_2H_5)_3SiCH_2CH(CH_3)CH_2CH=CH_2$		7,21	567	566	—1
$(CH_3)SiCH_2C_6H_5$ *		8,29	605*	—	—
$(C_2H_5)_3SiCH_2C_6H_5$		7,30	570	569	—1
$(CH_3)_3SiCH_2CH_2C_6H_5$ *		8,53	615*	—	—
$(C_2H_5)_3SiCH_2CH_2C_6H_5$		7,54	590	577	—13

* $\Sigma e_i = \Sigma e_i + (n-1)\, 0.77.$

TABLE 2 (continued)

Compound	Literature reference	Σe_i	$^v e$	$^v B$	Δ
$(CH_3)_2(C_2H_5)SiCH_2CH_2C_6H_5$		8,28	604	602	—2
$(CH_3)SiCH_2C(CH_3)=CH_2$ *		8,06	596*	—	—
$(CH_3)_2(C_2H_5)SiCH_2C(CH_3)=CH_2$		7,73	581	584	+3
$(C_2H_5)_3SiCH_2C(CH_3)=CH_2$	[21]	7,21	561	561	0
$(CH_3)_3SiCH=CH—CH=CH_2$ *		8,65	620*	—	—
$(CH_3)_2(C_2H_5)SiCH=C—CH=CH_2$		8,32	602	606	+4
$(CH_3)(C_2H_5)_2SiCH=C—CH=CH_2$		7,99	593	593	0
$(CH_3)_3SiCH_2CH=C=CH_2$ *		8,46	612*	—	—
$(CH_3)_2(C_2H_5)SiCH_2CH=C=CH_2$		8,13	603	599	—4
$(CH_3)(C_2H_5)_2SiCH_2CH=C=CH_2$		7,80	693	586	—7
$(CH_3)_3SiCH_2CH_2C\equiv CH$ *		7,93	591*	—	—
$(CH_3)_2(C_2H_5)SiCH_2CH_2C\equiv CH$		7,60	582	579	—3
$(CH_3)(C_2H_5)_2SiCH_2CH_2C\equiv CH$		7,27	573	568	—5
$(CH_3)_3SiCH=CH—CH_3$ *		8,53	615*	—	—
$(CH_3)_2(C_2H_5)SiCH=CH—CH_3$		8,20	597	602	+5
$(CH_3)_3Si—Br$	[22]	8,85	634	629	—5
$(CH_3)_3SiCH(CH_3)_2$ *		7,34	570*		

*$\Sigma e_i = \Sigma e_i + (n-1)\ 0.77$.

TABLE 3
Frequencies ν (Si-C) in the Allyl-Silanes

Compound	Σe_i	$^v e$	$^v B$	Δ
$Si(CH_2CH=CH_2)_4$	5,83	525	525	0
$(CH_3)Si(CH_2CH=CH_2)_3$	6,18	532	534	+2
$(CH_3)_2Si(CH_2CH=CH_2)_2$	6,53	543	544	+1
$(CH_3)_3SiCH_2CH=CH_2$*	6,88	555	555	0
$(C_2H_5)_3SiCH_2CH=CH_2$	5,89	543	527	—16
$(CH_3)_2(C_2H_5)SiCH_2CH=CH_2$	6,55	554	545	—9
$(CH_3)_2(C_6H_5)SiCH_2CH=CH_2$	7,46	570	574	+4
$(n\text{-}C_3H_7)Si(CH_2CH=CH_2)_3$	6,18	543	534	—9
$(n\text{-}C_3H_7)_3SiCH_2CH=CH_2$	6,88	556	555	—1
$(n\text{-}C_4H_9)_3SiCH_2CH=CH_2$	6,88	564	555	—9
$(CH_2=CH—CH_2)_2Si\begin{smallmatrix}CH_2—CH_2\\ \mid\\ CH_2—CH_2\end{smallmatrix}$	6,65	558	548	—10

*$\Sigma e_i = \Sigma e_i + (n-1)\ 0.77$.

Many projects have been carried out up to the present time (cf. for example, review [23]), in which the link has been established between the nature of the substituent and the chemical reactivity of the molecules, and therefore the quantitative characteristics of the properties of the radicals permit   a more complete understanding of the nature of the interactive effect of the atoms in the molecules, and of the regularities of their chemical structure. It may be possible to apply the regularities discovered to the study of other classes of organosilicon compounds, especially the chlorides and the hydride silanes. In addition to this, the agreement in principle

between our data and the results of the investigations of Bell and others cited above, makes it likely that other regularities of a more general nature will be discovered in compounds not so far investigated.

CONCLUSIONS

1. A relationship has been established between the nature of a radical, characterized by its effective electronegativity, and the frequency of the fully symmetrical valence oscillation of the Si-C bond.

2. The relationship discovered makes possible quantitative conclusions as to the nature of the intramolecular interactions of the silicon atom and the radicals with which it is combined.

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TAUTOMERISM OF CARBOTHIOIC ACIDS IN APROTIC MEDIA

S. T. Ioffe, Yu. N. Sheinker, and M. I. Kabachnik

Institute of Heteroorganic Compounds, Academy of Sciences, USSR;
S. Ordzhonikidze Scientific Research Institute of Chemistry and Pharmacy

In earlier investigations it was shown that the principal regularities of tautomeric equilibrium may be derived from the theory of acid-base protolytic equilibrium. Contrary to ordinary protolytic equilibrium

$$HA + S = A^- + HS^+,$$
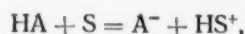
the lyonium ion (HS^+) in the tautomeric case is in equilibrium not with one, (HA), but two nonionized acid molecules (HA_1 and HA_2)

$$HA_1 + S = A^- + HS^+ = HA_2 + S.$$
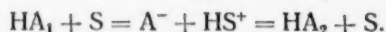
Correspondingly, the constant of tautomeric equilibrium in medium S (K_{TS}) may be expressed through the ionization constants of the tautomeric forms (K_{A_1S} and K_{A_2S}) or through their thermodynamic acidity constants (K_{a_1} and K_{a_2}) and the corresponding activity coefficients of the undissociated forms f_{1S} and f_{2S} [1]

$$K_{TS} = \frac{K_{A_1S}}{K_{A_2S}} = \frac{K_{a_1}}{K_{a_2}} \cdot \frac{f_{1S}}{f_{2S}}. \tag{1}$$

On passing from one solvent (S_1) to another (S_2) the ionization constants of the tautomeric forms change in conformity with the Brönsted-Izmailov rule

$$pK_{A_1S_1} = pK_{A_1S_2} + \text{const}, \tag{2}$$
$$pK_{A_2S_1} = pK_{A_2S_2} + \text{const}. \tag{3}$$

The constants of tautomeric equilibrium change correspondingly [2]:

$$pK_{TS_1} = pK_{TS_2} + \text{const}. \tag{4}$$

Application of the Brönsted-Izmailov theory [3] to tautomeric equilibria made it possible to find out certain basic regularities of the latter and to develop new experimental methods for determining the constants. One of these methods consists in determining the effective ionization constants of the tautomeric mixtures in two chosen solvents and comparing them with the ionization constants of certain model acids which are similar in structure to the tautomeric forms under investigation, but are not tautomeric. In pK_{AS1} and pK_{AS2} coordinates

(Fig. 1) the model substances give two parallel straight lines with a slope equal to unity, according to Formulas (2) and (3). Points, corresponding to tautomeric mixtures, fall in the region between these two straight lines. Knowing the coordinates of these points and the segments of the axis of ordinates, intercepted by the straight lines of the nontautomeric acids (standard lines), one can calculate the constants of tautomeric equilibrium [4]. Thus, for instance, the constants of tautomeric equilibrium of ketoenols [4] and organophosphorus thionethiols [5] were determined. In other cases points, corresponding to tautomeric substances, lay on one of the standard lines; this indicated a nearly complete shift of tautomeric equilibrium toward the form corresponding to this line. This was observed during investigations of lactim-lactam tautomerism [6] and tautomerism of the acid esters of alkylthiophosphinic acids [7].

It was of interest to extend the method set forth, to aprotic media. In solvents of this type acids and bases interact otherwise than in conducting protolytic media. According to Izmailov, all possible stages of protolytic interaction may be clearly expressed here: the formation of a complex of the acid with the base (hydrogen-bond formation), conversion of this complex to an ion pair (proton transfer), and finally dissociation of ion pairs with formation of solvated ions:

$$HA + B \rightleftarrows AH \ldots B \rightleftarrows [A^-HB^+] \rightleftarrows A^- + HB^+$$
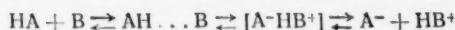
In conducting protolytic media with high dielectric constant (water) the concentration of complexes and ion pairs is low, and Brönsted equilibrium of the undissociated acid with the ions is practically attained. At intermediate values of the dielectric constant (alcohols) the role of ion pairs and, to a lesser degree, molecular complexes becomes appreciable. In aprotic media of low dielectric constant the last step—dissociation to free ions—practically does not occur.

In going over to the equilibrium of tautomeric acids in aprotic media, not only isomerism of undissociated molecules, but also isomerism of molecular complexes formed by undissociated tautomeric forms with a base—a proton carrier* —must be assumed. In the ion-pair stage, however, isomerism vanishes ("common ion"), and the ion pair must be in equilibrium with both tautomeric forms. Thus tautomeric equilibrium in aprotic media may be represented by the following scheme: * *

$$HA_1 + B \rightleftarrows A_1H \ldots B \rightleftarrows [A^-HB^+] \rightleftarrows A_2H \ldots B \rightleftarrows HA_2 + B$$
$$\downarrow\uparrow$$
$$A^- + HB^+$$
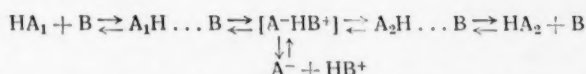
When the dielectric constant of the solvent (benzene) is low, the last stage—dissociation into ions—apparently can safely be neglected. In this case the constant of tautomeric equilibrium may be expressed through the constants of protolysis of the tautomeric forms by base B (cf. [1])

$$K_{TS} = \frac{K_{p_1B}}{K_{p_2B}} \tag{5}$$

As we recently showed [8], the protolysis constants can be determined conveniently by using as protolyte, an indicator, added in stoichiometric quantities. Using the base of crystal violet as indicator, we investigated the protolysis of carboxylic acids in benzene and chlorobenzene and found that interaction of the base with carboxylic acids leads to the formation of a hydrated ion pairs ($RCOO^- \cdot Ar_3C^+ \cdot H_2O$). Protolysis constants were calculated by the formula

$$K_{pB} = \frac{f^n}{(a_0 - f)(b_0 - f)}, \tag{6}$$

where f is the concentration of colored particles, determined photocolorimetrically, a_0 and b_0 are the initial concentrations of acid and base, and n is an exponent characterizing the number of particles in equilibrium with acid and base. Within the limits of experimental error, n in benzene and chlorobenzene was invariably found to be equal to unity (see Table 1). The protolysis constants thus found are well described by the relation,

---

*In aprotic media the role of proton carrier may be played either by molecules of any base present in solution, or the tautomeric-acid molecules themselves, to the extent of their basic properties (autoprotolysis).
** Here we are concerned with the forms of particles in equilibrium, and not the mechanism of proton transfer. That is a separate problem.

$$(pK_{pB})_{S_1} = (pK_{pB})_{S_2} + \text{const}, \qquad (7)$$

analogous to the Brönsted relation for ionic dissociation.

This last fact makes it possible to apply to tautomeric acids the method of determining constants of tautomeric equilibrium, set forth above and based on the measurement of ionization constants in two solvents. We used it to study the tautomerism of carbothioic acids

$$R-C\underset{SH}{\overset{O}{\lessgtr}} \rightleftarrows R-C\underset{OH}{\overset{S}{\lessgtr}}$$

$$\text{(I)} \qquad\qquad \text{(II)}$$

in benzene and chlorobenzene.

Fig. 1. Principle of the potentiometric method of determining constants of tautomeric equilibrium.
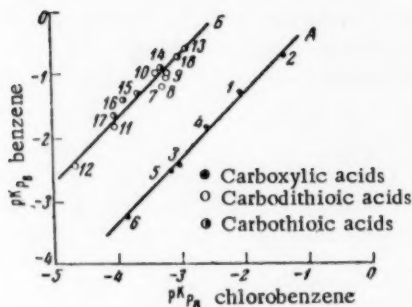
Fig. 2. Constants of protolysis of acids by the base of crystal violet in benzene and chlorobenzene: 1) Acetic; 2) propionic; 3) formic; 4) benzoic; 5) p-bromobenzoic; 6) p-trifluoromethylbenzoic; 7) dithioacetic; 8) dithiopropionic; 9) dithiobutyric; 10) dithiovaleric; 11) dithio-p-toluic; 12) dithio-p-bromobenzoic; 13) thioacetic; 14) thiobenzoic; 15) p-bromothiobenzoic; 16) p-trifluoromethylthiobenzoic; 17) p-nitrothiobenzoic; 18) thio-p-toluic.

The tautomeric equilibrium of carbothioic acids was studied by Hantzsch and Scharf [9] by means of the ultraviolet spectra; they showed that the equilibrium of thioacetic acid is shifted toward form (I). On comparison of the absorption spectra of thiobenzoic acid with those of S-methyl thiobenzoate in ether and thiobenzamide in water the hypothesis was advanced, that in aqueous solution the equilibrium is shifted toward form (I), whereas in alcoholic solution it is shifted toward form (II). Bloch, whose studied the infrared spectra of thioacids [10], did not find hydroxyl-group absorption frequencies; this also indicated the predominance of form (I). Crouch [11] did not find any absorption in the $2.9\ \mu$ (OH group) or $10.4\ \mu$ (C=S group) region of the infrared spectrum of thioacetic acid, but found strong absorption in the $3.9\ \mu$ region (SH group), indicating the presence of form (I). Sheppard [12] reached a similar conclusion on investigating the infrared spectra of thioacetic acid. However, Mecke and Spiesecke [13] found an OH valence-vibration band in the infrared spectra of thioacetic acid at an elevated temperature; on this basis the authors concluded that tautomeric equilibrium existed between forms (I) and (II). Sjöberg [14] observed a weak absorption in the region of C=S valence vibrations (1225 cm^{-1}) in the case of a thin layer of trichlorothioacetic acid, which grew stronger with increase of temperature and was ascribed by the author to the thiono form. At the same time solutions of the acid in carbon disulfide gave spectra similar to those of trichloroacetyl chloride solutions. This indicated that only form (I) was present in solution.

Our method of investigation requires the use of nontautomeric model acids of the same chemical type as the tautomeric forms being studied. As standard substances of this kind we used: carbodithioic acids $R-C\underset{SH}{\overset{S}{\lessgtr}}$ for form (I) and carboxylic acids $RC\underset{OH}{\overset{O}{\lessgtr}}$ for form (II). The constants of protolysis of carboxylic, carbothioic, and carbodithioic acids by the base of crystal violet in benzene and chlorobenzene were determined by the method described earlier [8]. As the results of calculations based on colorimetric data (method of least squares) showed, the exponent $\underline{n}$ in Formula (6) for carbothioic and carbodithioic acids is equal to unity in all cases, within the

TABLE 1

Constants of Protolysis of Acids by the Base of Crystal Violet in Benzene
and Chlorobenzene

Number on graph	Acid	n		pK_{pB}	
		benzene	chloro-benzene	benzene	chloro-benzene
1	CH_3COOH	0,98	1,00	—1,24	—1,96
2	C_2H_5COOH	1,03	1,07	—0,67	—1,27
3	$HCOOH$	1,08	1,10	—2,42	—2,96
4	C_6H_5COOH	0,95	0,96	—1,79	—2,51
5	$p\text{-}BrC_6H_4COOH$	0,95	1,00	—2,50	—3,13
6	$p\text{-}CF_3C_6H_4COOH$	1,03	1,04	—3,22	—3,85
7	CH_3CSSH	1,02	1,11	—1,15	—3,24
8	C_2H_5CSSH	1,06	1,10	—0,94	—3,18
9	$n\text{-}C_3H_7CSSH$	1,08	1,10	—0,92	—3,18
10	$n\text{-}C_4H_9CSSH$	1,08	1,10	—0,92	—3,30
11	$p\text{-}CH_3C_6H_4CSSH$	1,05	1,03	—1,78	—4,00
12	$p\text{-}BrC_6H_4CSSH$	1,01	1,01	—2,38	—4,63
13	CH_3COSH	1,05	1,04	—0,60	—2,89
14	C_6H_5COSH	1,02	1,00	—0,86	—3,23
15	$p\text{-}BrC_6H_4COSH$	0,99	0,99	—1,24	—3,62
16	$p\text{-}CF_3C_6H_4COSH$	1,01	1,01	—1,36	—3,84
17	$p\text{-}O_2NC_6H_4COSH$	1,02	0,96	—1,61	—4,00
18	$p\text{-}CH_3C_6H_4COSH$	1,03	1,02	—0,73	—3,00

limits of experimental error (see Table 1). It follows from this that, similarly to the case of carboxylic acids [8], salt formation by the base of crystal violet with carbothioic and carbodithioic acids in benzene and chlorobenzene, is accompanied by the formation of a hydrated ion pair (single particle). Values of pK_p for protolysis are given in Table 1. When values of pK_{pB} for the investigated acids in benzene (axis of ordinates) and chlorobenzene (axis of abscissas) are plotted on a graph (Fig. 2), points 1-6, corresponding to straight line A, which has a slope of 1.01, are obtained for carboxylic acids. Similarly points 7-12, corresponding to straight line B, which has a slope of 0.997, are obtained for carbodithioic acids. This indicates that Equation (7), analogous to the Brönsted relation for ionic dissociation, is valid for carbodithioic acids. Points 13-18, corresponding to carbothioic acids within the limits of experimental error, lie near straight line B, which indicates that the equilibrium is substantially shifted toward tautomeric form (I). Points 13-18 are too close to straight line B to permit quantitative calculation of tautomeric equilibrium.

As one of us, Mastryukova, Shipov, and Melent'eva showed [15], pK_{AS} is a linear function of σ (Hammett's equation) for tautomeric substances with equilibrium positions substantially shifted toward one of the tautomeric forms. On constructing the graph for carbothioic acids in benzene and chlorobenzene in the coordinates, pK_{pB} and Hammett's σ, we obtained good agreement with the linear functionality (Fig. 3); this also confirms the absence of any appreciable amounts of a second tautomeric form in equilibrium.

In order to confirm the obtained data by an independent method, we investigated the ultraviolet absorption spectra of solutions of the studied substances in benzene and chlorobenzene. To reach the necessary conclusions on equilibrium in these solutions, the ultraviolet spectra of the tautomeric acids were compared with those of carbothioic esters alkylated on sulfur ($C_6H_5COSCH_3$, $p\text{-}NO_2C_6H_4COSCH_3$, $p\text{-}BrC_6H_4COSCH_3$) and therefore corresponding in structure to tautomeric form (I), and esters alkylated on oxygen ($C_6H_5CSOC_2H_5$, $p\text{-}NO_2C_6H_4CSOC_2H_5$, $p\text{-}BrC_6H_4CSOC_2H_5$) and corresponding to tautomeric form (II). The spectra of these model compounds for thiobenzoic acid were obtained both in benzene and chlorobenzene solutions and in alcoholic and dioxane ones. Consideration of the data shows that the spectra are the same in all solvents (in the region in which benzene and
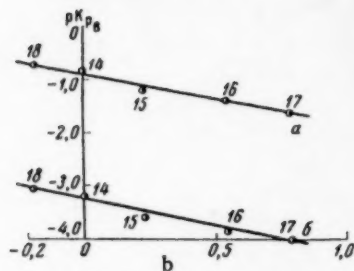
Fig. 3. Relation between pK_{pB} and Hammett's σ for carbothioic acids in benzene (a) and chlorobenzene (b). The symbols and point numbers have the same significance as in Fig. 2.
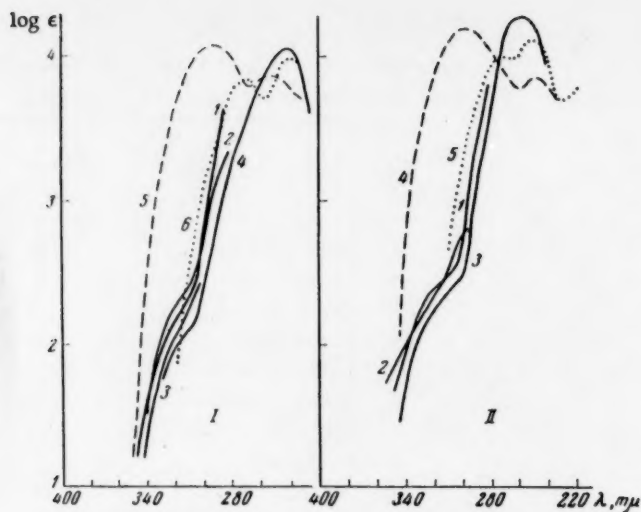
Fig. 4. Ultraviolet absorption spectra: I. 1) Thio-p-toluic acid in benzene; 2) thiobenzoic acid in benzene; 3) same in chlorobenzene; 4) same in heptane; 5) O-ethyl thiobenzoate; 6) S-methyl thiobenzoate. II. 1) p-Bromothiobenzoic acid in benzene; 2) same in chlorobenzene; 3) same in heptane; 4) O-ethyl p-bromothiobenzoate; 5) S-methyl p-bromothiobenzoate.

chlorobenzene are sufficiently transparent, at least). The two series of model compounds differ appreciably in their spectra: Absorption maxima in the 240-270 mμ region are characteristic of S-substituted esters, whereas the absorption maxima for O-substituted esters lie in the 290-300 mμ region.
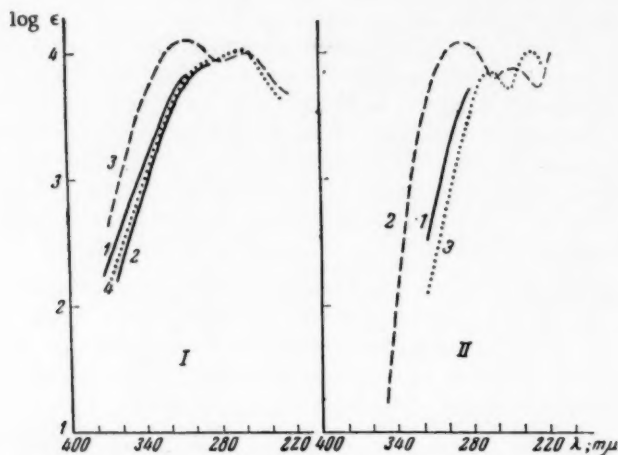
Fig. 5. Ultraviolet absorption spectra: I. 1) p-Nitrothiobenzoic acid in chlorobenzene; 2) same in benzene; 3) O-ethyl p-nitrothiobenzoate; 4) S-methyl p-nitrothiobenzoate. II. 1) p-Trifluoromethylthiobenzoic acid in benzene; 2) O-ethyl thiobenzoate; 3) S-methyl thiobenzoate.

Comparison of the spectra of tautomeric thioacids with the spectra of their esters, as is evident from Fig. 4, confirms the results obtained by the indicator method, with regard to the shift of tautomeric equilibrium of carbothioic acids dissolved in benzene and chlorobenzene, toward form (I). The spectra of thiobenzoic acids in the region accessible for the measurement of spectra in these solvents ($\lambda > 280$ mμ), are similar to those of their S-alkyl-substituted esters, and sharply differ from the spectra of their O-esters.*

In the spectra of thiobenzoic, p-bromothiobenzoic, and thio-p-toluic acids in the region near 300 mμ (where the absorption maximum of the O-alkyl-substituted esters occurs), however, some absorption is observed in the form of a shoulder on the descending branch of the curve. If it is assumed that this absorption is determined by the presence of tautomeric form (II), the content of this tautomeric form can be estimated, from the absorption intensity in this region, to be about 1-2% (somewhat more for the p-CH$_3$ derivative, and somewhat less for thiobenzoic acid itself)**. In compounds in which CF$_3$ and NO$_2$ groups occur as substituents in the para-position of the phenyl nucleus, no such shoulder is found on the curve (Fig. 5).

EXPERIMENTAL***

The carbodithioic acids were prepared by treating the corresponding Grignard reagents with carbon disulfide [16]. The carbothioic acids were prepared by treating carboxylic acid chlorides with potassium hydrosulfide [17]. The carbothioic esters alkylated on sulfur, which were required for the spectral investigations, were prepared by treating the potassium salts of the acids with methyl iodide [18, 19], whereas the carbothioic esters alkylated on oxygen were prepared by treating benzimido alkyl ethers with hydrogen sulfide [20]. The constants of the substances synthesized are compared with literature data in Table 2.

p-Trifluoromethylthiobenzoic acid. A solution of 2.8 g of potassium hydroxide in 50 ml of alcohol was saturated with hydrogen sulfide, with cooling, until it gave a negative reaction with phenolphthalein. A solution of 5.2 g of p-trifluoromethylbenzoyl chloride (b.p. 184-186°) in 20 ml of benzene was added to the solution dropwise at -10°. Then the mixture was stirred for 45 min at -10°. The potassium chloride was filtered out (1.9 g). The solvent was distilled from the filtrate in vacuo, and the residue (4.7 g) was dissolved in water. The aqueous solution was extracted with ether and then acidified with dilute hydrochloric acid. The oil which separated was extracted with ether. After drying, the ether was distilled off. The residual oil crystallized on cooling. After recrystallization from hexane there were obtained 1.4 g of p-trifluoromethylbenzoic acid, m.p. 210-211°, and 0.4 g of p-trifluoromethylthiobenzoic acid, m.p. 118-120°. Found: F 27.50; 27.75%. C$_8$H$_5$F$_3$OS. Calculated: F 27.65%.

O-Ethyl Thiobenzoate. Into a solution of 8 g of benzimido ethyl ether [b.p. 101-102° (15 mm)] [29] in 20 ml of absolute ether, a current of dry hydrogen sulfide was passed, with cooling, for 30 hours, until ammonia ceased to be evolved. After driving off the ether and distillation in vacuo there was obtained 2.5 g (28%) of O-ethyl thiobenzoate, b.p. 80-83° (3 mm), 110-112° (11 mm), n_D^{20} 1.5920; d_4^{20} 1.1422. Found: C 65.18; 65.28; H 5.99; 6.06; S 19.13; 19.20%; MR 49.18. C$_9$H$_{10}$OS. Calculated: C 65.00; H 6.07; S 19.30%; MR 49.20. Literature data [20] for O-ethyl thiobenzoate: b.p. 124-125° (3-5 mm); d_4^{20} 1.0452, apparently are incorrect.

O-Ethyl p-Nitrothiobenzoate. An 0.8 g quantity of p-nitrobenzimido ethyl ether (m.p. 76-78° [30]) was dissolved in 10 ml of absolute ether at room temperature, and hydrogen sulfide was passed through the mixture for 3 weeks, until ammonia ceased to be evolved (absolute ether was added at intervals). The ether was distilled off and the residual crystals recrystallized from hexane; yield 0.5 g (50%); m.p. 101-103° (with decomposition). Found: C 51.40; 51.30; H 4.37; 4.31; S 14.77; 14.85%. C$_9$H$_9$NO$_3$S. Calculated: C 51.17; H 4.29; S 15.18%.

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*It should be noted that the attachment of a CH$_3$ group to a S atom (in S-substituted esters) apparently has a greater effect on the spectra than is usually observed on substitution of a hydrogen atom by alkyl groups, on O (or N) atoms. In connection with this, certain differences are observed in the spectra of thiobenzoic acids in solvents of low polarity (benzene, chlorobenzene, n-heptane), and S-methyl-substituted esters of these acids: The latter have a rather broad, doubled absorption band with two maxima (at 235 and 265 mμ), while the thiobenzoic acids themselves usually have a somewhat narrower band in heptane with one maximum in the 240-260 mμ region.

** The result obtained does not contradict the data of the indicator method, since the small content of tautomeric form (II) could escape notice.

*** With the participation of L. A. Bogdanova.

TABLE 2

Properties of the Substances Investigated

Substance	Constants obtained	Literature data
CH_3CSSH	B.p. 35° (15 mm), d_4^{20} 1.2458	B.p. 37° (17 mm), d_4^{20} 1.24 [16]
C_2H_5CSSH	B.p. 51° (21 mm), d_4^{20} 1.1266	B.p. 48° (17 mm), d_4^{20} 1.12 [16]
n-C_3H_7CSSH	B.p. 57° (12 mm), d_4^{20} 1.1164	B.p. 59° (13 mm), d_{19} 1.08 [16]
n-C_4H_9CSSH	B.p. 96-97° (34 mm), d_4^{20} 1.1155	
p-$CH_3C_6H_4CSSH$	M.p. 38-39°	M.p. 40° [21]
p-BrC_6H_4CSSH	M.p. 35-36°	M.p. ~35° [22]
CH_3COSH	B.p. 92-93°	B.p. 88-91.5° [23]
C_6H_5COSH	B.p. 95-97° (15 mm), n_D^{20} 1.6030	B.p. 95-97° (15 mm) n_D^{20} 1.6030 [24]
p-BrC_6H_4COSH	M.p. 79-80°	M.p. 78-79° [25]
p-CF_3C_6COSH	M.p. 118-120°	
p-$O_2NC_6H_4COSH$	M.p. 92-93°	M.p. 90-95° [18]
p-$CH_3C_6H_4COSH$	M.p. 43-45°	M.p. 43-44° b.p. 131° (15 mm) [26]
p-BrC_6H_4COOH	M.p. 251-252°	M.p. 250-251° [27]
p-$CF_3C_6H_4COOH$	M.p. 214-215°	M.p. 212-213° [28]
$C_6H_5C \overset{O}{\underset{SCH_3}{}}$	B.p. 115-116° (20 mm)	B.p. 134° (25 mm) [19]
$C_6H_5C \overset{S}{\underset{OC_2H_5}{}}$	B.p. 80-83° (3 mm), 110-112° (11 mm), n_D^{20} 1.5920 d_4^{20} 1.1422	B.p. 124-127° (3-5 mm) d_4^{20} 1.0452 [20]
p-$NO_2C_6H_4C \overset{O}{\underset{SCH_3}{}}$	M.p. 96-97°	M.p. 96-97° [18]
p-$NO_2C_6H_4C \overset{S}{\underset{OC_2H_5}{}}$	M.p. 101-103° (with decompn.)	—
p-$BrC_6H_4C \overset{O}{\underset{SCH_3}{}}$	M. p. 34° B.p. 102-104° (3 mm)	—
p-$BrC_6H_4C \overset{NH}{\underset{OC_2H_5}{}}$	B.p. 107-108° (3 mm) n_D^{20} 1.5739, d_4^{20} 1.4195	—
p-$BrC_6H_4C \overset{S}{\underset{OC_2H_5}{}}$	B.p. 96° (1 mm) M.p. 41°	—

S-Methyl p-Bromothiobenzoate. One g of p-bromothiobenzoic acid was dissolved in 20 ml of absolute ether, and 0.43 g of potassium hydroxide in 5 ml of alcohol was added, with cooling. After distilling off the alcohol in vacuo, potassium p-bromothiobenzoate was obtained; yield 1.1 g; it did not melt below 250°. To the light-green solution of 1.1 g of the potassium salt in 20 ml of absolute alcohol, 1 g of methyl iodide was added: the mixture was heated for 45 min in a boiling water bath. Fifty ml of water was added to the slightly-turbid solution. The oil which separated was extracted with ether. After drying, driving-off of ether, and distillation there was obtained 0.5 g (47%) of a substance with b.p. 102-104° (3 mm); m.p. 34°. Found: C 41.78; 41.96; H 3.11; 3.07; Br 34.96; 34.73%. C_8H_7BrOS. Calculated: C 41.57; H 3.06; Br 34.58%.

p-Bromobenzimido Ethyl Ether. Ten g of p-bromobenzonitrile [31] (m.p. 112-112.5°) was dissolved in 150 ml of absolute alcohol, and a current of dry HCl was passed through the mixture for 6 hours, the latter being cooled with ice water. The solution was left in a refrigerator for 3 days. After driving off the alcohol, the residual crystals were washed with ether. There was obtained 11.9 g (82%) of p-bromobenzimido ethyl ether hydrochloride; m.p. 180-181°. Found: N 5.43; 5.51%. $C_9H_{11}OBrClN$. Calculated: N 5.30%.

An 11.1 g quantity of the hydrochloride was treated with 20% potash solution. The colorless oil which separated was extracted with ether, and the solution was dried with potash and distilled. There was obtained 8.4 g (88.5%) of p-bromobenzimido ethyl ether; b.p. 107-108° (3 mm), n^{20}_D 1.5739; d_4^{20} 1.4195. Found: N 6.32; 6.40%. $C_9H_{10}OBrN$. Calculated %: N 6.14.

O-Ethyl p-Bromothiobenzoate. A solution of 6.5 g of p-bromobenzimido ethyl ether in 50 ml of absolute ether was saturated at room temperature with dry hydrogen sulfide for 24 hours, until ammonia ceased to be evolved. The yellow ethereal solution was washed with water until it gave a neutral reaction. The ether layer was dried with sodium sulfate and the ether distilled off. The residue crystallized. There was obtained 6.8 g (98.5%) of lemon-yellow crystals; b.p. 96° (1 mm), m.p. 41°. Found: C 44.28; 44.21; H 3.75; 3.85; Br 32.65; 32.62%. C_9H_9BrOS. Calculated: C 44.09, H 3.70; Br 32.60%.

Colorimetric and Spectral Measurements. Colorimetric measurements in benzene and chlorobenzene were performed by means of an FEK-M electrophotocolorimeter. For the measurement procedure and method of calculation, see [8]. The ultraviolet absorption spectra of solutions in heptane, benzene, and chlorobenzene were obtained with an SF-4 spectrophotometer.

SUMMARY

1. The constants of protolysis of carbothioic and carbodithioic acids by the base of crystal violet in benzene and chlorobenzene, were determined by a colorimetric method. In aprotic solvents neutralization of these acids by a base leads to the formation of ion pairs which do not dissociate appreciably. Values of the exponent n, which characterizes the number of particles in equilibrium with acid and base, are close to unity.

2. The protolysis constants, found for carbodithioic acids in benzene and chlorobenzene, satisfy an equation analogous to Brönsted's equation for ionic dissociation. This permits the use of protolysis constants to determine constants of tautomeric equilibrium.

3. The tautomeric equilibrium of carbothioic acids in benzene and chlorobenzene was investigated by the indicator method and by means of ultraviolet spectra. It was shown that the tautomeric equilibrium of carbothioic acids in benzene and chlorobenzene is substantially shifted toward the thiol forms.

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TAUTOMERISM OF CARBOTHIOIC ACIDS IN PROTOLYTIC MEDIA

Yu. N. Sheinker, S. T. Ioffe, and M. I. Kabachnik

S. Ordzhonikidze Scientific Research Institute of Chemistry and Pharmacy
Institute of Heteroorganic Compounds, Academy of Sciences, USSR

In the preceding article [1] we showed by the indicator method and by means of ultraviolet spectra, that the tautomeric equilibrium of carbothioic acids

$$RC\underset{SH}{\overset{O}{\lessgtr}} \rightleftarrows RC\underset{OH}{\overset{S}{\lessgtr}}$$

$$(I) \qquad (II)$$
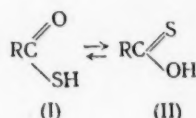
in aprotic media—benzene and chlorobenzene—is substantially shifted toward the thiol forms (I). It did not prove possible to evaluate the content of thiono forms (II) quantitatively. True, some absorption was observed in the form of a shoulder on the descending branch of the curve in the region near 300 mμ in the spectra of thiobenzoic, p-bromothiobenzoic, and thio-p-toluic acids in benzene and chlorobenzene. Since absorption in this region is characteristic of O-substituted (thiono) esters, the presence of 1-2% thiono forms in equilibrium with 98-99% thiol forms could be suspected. It was of interest to attempt to shift the equilibrium position toward the thiono forms by using more polar solvents. Investigation of the tautomeric equilibrium of carbothioic acids in aqueous media by the potentiometric method [2], which we used successfully in the study of other forms of tautomerism, would be difficult owing to the tendency of these substances to hydrolyze, hydrogen sulfide being evolved. We investigated these substances in the solid and liquid states by means of infrared spectra and in alcoholic and dioxane solutions by means of ultraviolet spectra. As in the preceding article, the spectra of the tautomeric substances were compared with the spectra of their O- and S-substituted esters.

On comparison of spectra, obtained in alcoholic and dioxane solutions, with the spectra of benzene and chlorobenzene solutions, it was found that the above-mentioned slight absorption in the region near 300 mμ, observed in the spectra of thiobenzoic, p-bromothiobenzoic, and thio-p-toluic acids in benzene and chlorobenzene increased sharply in dioxane and even more in alcoholic solutions. The form of the absorption curves was substantially changed; in character they became appreciably more like the absorption curves of O-alkyl-substituted esters (Fig. 1). For derivatives in which CF$_3$ and NO$_2$ groups occurred in the para-position of the phenyl nucleus, no such change in the spectra was observed; the absorption curves in these solvents coincided quite well with those of model compounds of the thiol tautomeric form (I) (S-methyl esters) (Fig. 2). Thus the specific absorption in the 300 mμ region is determined by the thiono tautomeric form (II), which is in equilibrium with form (I); although the equilibrium is strongly shifted toward form (I) in solvents of low polarity (benzene, chlorobenzene), the content of form (II) approaches or even exceeds the content of form (I) in dioxane and alcohol.

It also follows from these data, that the introduction of strongly electrophilic substituents (NO$_2$, CF$_3$) into the aromatic nucleus, leads to such a pronounced shift of the position of tautomeric equilibrium (toward form I),
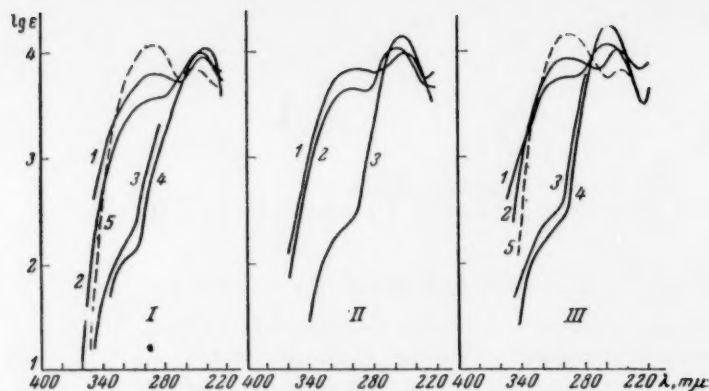
Fig. 1. Ultraviolet absorption spectra: I. Thiobenzoic acid: 1) in ethyl alcohol; 2) in dioxane; 3) in benzene; 4) in heptane; 5) O-ethyl thiobenzoate. II. Thio-p-toluic acid: 1) in ethyl alcohol; 2) in dioxane; 3) in heptane. III. p-Bromothiobenzoic acid: 1) in ethyl alcohol; 2) in dioxane; 3) in benzene; 4) in heptane; 5) O-ethyl p-bromothiobenzoate.
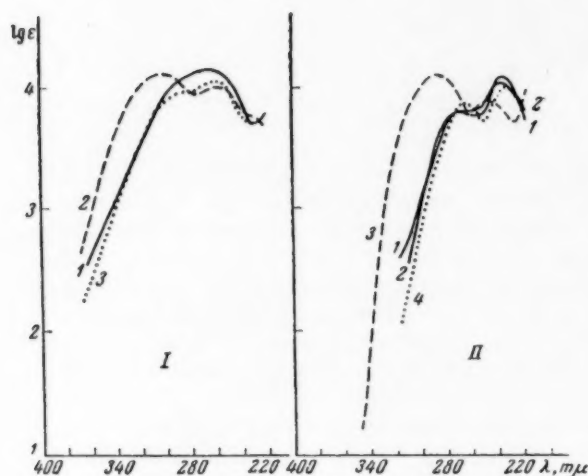
Fig. 2. Ultraviolet absorption spectra: I. p-Nitrothiobenzoic acid: 1) in dioxane; 2) O-ethyl p-nitrothiobenzoate; 3) S-methyl p-nitrothiobenzoate. II. p-Trifluoromethylthiobenzoic acid: 1) in ethyl alcohol; 2) in dioxane; 3) O-ethyl thiobenzoate; 4) S-methyl thiobenzoate.
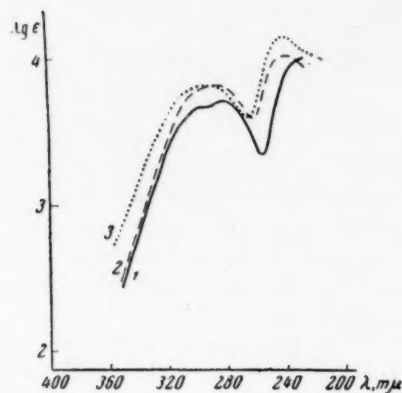
Fig. 3. Ultraviolet absorption spectra of carbothioic acids in a 0.1 N alcoholic sodium ethoxide sodium: 1) Thiobenzoic acid; 2) thio-p-toluic acid; 3) p-bromothiobenzoic acid.

that the equilibrium quantity of form (II) cannot be determined in any solutions by spectroscopic methods. On the other hand, introduction of electrodotic substituents (e.g., CH_3) into thiobenzoic acid shifts the equilibrium toward a higher content of form (II); this is especially noticeable in dioxane and alcoholic solutions. For the resulting compound, as well as for thiobenzoic acid itself and p-bromothiobenzoic acid, the content of tautomeric forms in the solutions can be approximately evaluated by means of the spectra. In the table, the content of tautomeric form (II), so calculated, is given in percentages in comparison with the data for benzene and chlorobenzene solutions, obtained earlier.

On analyzing the data obtained, it must be remembered that estimates of the content of tautomeric forms in the compounds considered, based on spectra, may contain certain errors. These errors may be determined by

Substance	Content of form (II) in %		
	benzine-chloro-benzene	diox-ane	alco-hol
C_6H_5COSH	~1	25	48
p-BrC_6H_4COSH	~1—1,5	36	56
p-$CH_3C_6H_4COSH$	~2	38	62
p-$CF_3C_6H_4COSH$	0	0	0
p-$NO_2C_6H_4COSH$	0	0	0

two circumstances. On the one hand, as we pointed out in the preceding article, the spectra of S-methyl-substituted esters (model compounds of thiol forms) differ somewhat from those of carbothioic acids in such a solvent as n-heptane. In connection with this, in calculating the constants of tautomeric equilibrium the absorption of the thiol tautomeric form was estimated not from the spectra of the S-methyl esters, but from the spectra of the acids themselves in heptane solution, in which, as was indicated earlier, the acids exist practically entirely in the thiol form. Thus, in calculating equilibrium constants in alcoholic and dioxane solutions we used data obtained for heptane solutions, which may lead to errors in calculation. On the other hand, the possibility of ionization of carbothioic acids under the conditions of measurement, was not taken into account in the calculation. Allowing for the rather high acidity of thioacids (pK_a in water is of the order of 4) and the use of very high dilutions ($V = 10^4$) in measuring the spectra, it can be assumed that in such a solvent as alcohol the degree of ionization may reach 10-15%.

Our measurement of the spectra of thioacids in a 0.1 N alcoholic sodium ethoxide solution, where the acids are obviously present entirely in the form of the anions, showed (Fig. 3) that thioacid anions have considerable absorption in that spectral region where the characteristic band of the thiono form occurs. In connection with this, the presence of the indicated quantities of ions in the solutions, may lead to high values of the content of the tautomeric form on calculation, although this, evidently, can happen only with alcoholic solutions, since the degree of ionization in dioxane must be considerably less.

We investigated the infrared spectra of aromatic carbothioic acids, as well as trifluorothioacetic acid, synthesized by us, which has not been described before in the literature. Infrared spectral data for these compounds in the free state (Fig. 4) (C_6H_5COSH and CF_3COSH as liquids, the rest as crystals) indicate that all the compounds under investigation exist in the thiol form under these conditions. This follows from the presence in the spectra, of bands in the 2500-2600 cm^{-1} region, characteristic of SH groups, intense carbonyl bands at 1670-1710 cm^{-1}, and the absence of bands in the 3000-3600 cm^{-1} region, which would characterize OH groups. True, in a thick layer of trifluorothioacetic acid a weak absorption is observed in the region of hydroxyl bands, which may be regarded either as an indication of small equilibrium quantities of the thiono form, or as a result of the presence of small amounts of hydroxyl-containing admixtures. We are inclined toward the latter point of view. It is interesting, that in the case of the two compounds $CF_3C_6H_4COSH$ and $NO_2C_6H_4COSH$ the thiol band is not found in the spectra. However, the presence of intense C=O bands at 1700 cm^{-1} and the total absence of absorption characteristic of OH groups, indicate that the thiol structure is retained in these substances.

EXPERIMENTAL

Trifluorothioacetic Acid. Seventeen g of trifluoroacetic acid was heated for 60 hours in a sealed tube at 120-130° with 8 g of phosphorus pentasulfide and 25 g of naphthalene. After the tube was opened, its contents were distilled in a water bath. There was obtained 4 g (20.6%) of trifluorothioacetic acid, b.p. 37.5-38.5° (732 mm), n_D^{20} 1.3420; d_4^{20} 1.4035; a very volatile liquid with a sharp, unpleasant odor. Found: C 18.93; 18.65; H 0.85; 0.89; F 44.58; 44.34%. C_2HF_3OS. Calculated: C 18.46; H 0.77; F 43.82%. Found MR 19.52; Calculated: MR

for $CF_3C\overset{O}{\underset{SH}{\parallel}}$ 19.76; and for $CF_3C\overset{S}{\underset{SH}{\parallel}}$ 20.29.
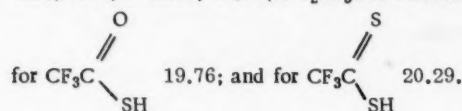
The syntheses of all the rest of the compounds are described in the preceding article [1].

The infrared spectra were taken with an IKS-11 spectrometer using a NaCl prism. The solids were examined in the form of a suspension (paste) in vaseline, and the liquids, in the form of layers 0.01-0.05 mm thick. The ultraviolet absorption spectra were obtained by means of an SF-4 spectrometer.
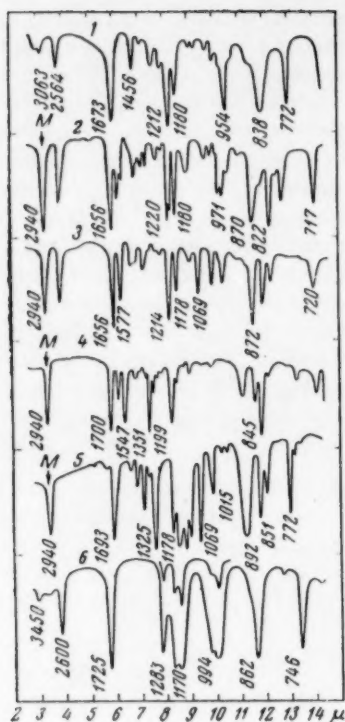
Fig. 4. Infrared spectra of carbothioic
acids: 1) Thiobenzoic acid (liquid);
2) thio-p-toluic; 3) p-bromothiobenzoic;
4) p-nitrothiobenzoic; 5) p-trifluoro-
methylthiobenzoic (all in crystals); 6)
trifluorothioacetic (liquid); the letter
M denotes the vaselin band.

SUMMARY

1. The infrared spectra of liquid or solid aromatic carbo-
thioic acids indicate their thiol structure.

2. In dioxane and especially in alcoholic solutions of thio-
benzoic acid and derivatives of the latter containing electro-
dotic substituents, the content of thiono forms, according to ul-
traviolet spectral data, approaches or even exceeds the content
of thiol forms.

3. The introduction of strongly-electrophilic substituents
(NO_2, CF_3) in the aromatic nucleus leads to such a great shift
of the equilibrium toward thiol forms, that the equilibrium
content of thiono forms cannot be detected in any solutions by
spectroscopic methods.

4. Trifluorothioacetic acid was synthesized; its structure
according to data on infrared spectra and molar refraction,
corresponds to the thiol form.

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CONDENSATION OF PHENOLS WITH 1,1,1-TRICHLOROPROPENE
AND 1,1,3-TRICHLOROPROPENE-1

N. A. Semenov and R. Kh. Freidlina

Institute of Heteroorganic Compounds, Academy of Sciences, USSR
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In one of our preceding articles [1] we described the condensation of phenol with 1,1,1-trichloropropene and 1,1,3-trichloropropene-1 on heating with and without $AlCl_3$. The structures of o-$HOC_6H_4CH_2CH=CCl_2$ and p-$HOC_6H_4CH_2CH=CCl_2$ were ascribed to the compounds obtained, on the basis of the fact that oxidation of their methyl ethers gave ortho-methoxybenzoic and anisic acids, respectively. At the same time it was shown that the reaction of 1,1,1-trichloropropene with sodium phenoxide takes place both at the "C" and the "O", and a neutral product was isolated, to which the structure of 1,1-dichloro-3-phenoxypropene-1 was ascribed. When 1,1,1-trichloropropene was replaced by 1,1,3-trichloropropene-1 in the reactions with phenol and sodium phenoxide, the same compounds were obtained.

Recently Kooijman and Wagner [2] studied the reaction of sodium phenoxide with 1,1,1,3-tetrachlorobutene. The authors investigated the reaction products by means of their infrared spectra and found that just as in the case studied by us, an ether having the structure

$$C_6H_5OCH-CH=CCl_2$$
$$|$$
$$CH_3$$
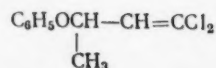
is formed, as well as ortho- and para-isomers of a substituted phenol having the structure $HOC_6H_4CH-CH=CCl_2$,

$$|$$
$$CH_3$$

the ortho-isomer being obtained in much greater quantity than the para-isomer. Different results were reported in the interesting work by Kotlyarevskii and Korbukh [3]. According to these authors' data, the reaction of sodium phenoxide with 1,1,1-trichloropropene goes otherwise than that with 1,1,3-trichloropropene-1; in the first case the compounds $C_6H_5OCCl_2-CH=CH_2$ and p-$HOC_6H_4CCl_2CH=CH_2$ are formed, whereas $C_6H_5OCH_2CH=CCl_2$ and p-$HOC_6H_4CH_2-CH=CCl_2$ are formed in the second case; they did not isolate ortho-substituted phenols in either case.

In the present article we describe the condensation of phenol with 1,1,3-trichloropropene-1 and subsequent isolation of ortho- and para-substituted phenols having the structure $HOC_6H_4CH_2CH=CCl_2$, identical in their constants with the corresponding compounds obtained by condensation of phenol with 1,1,1-trichloropropene and described by us earlier [1]. Furthermore, we carried out the interaction of 1,1,1-trichloropropene and 1,1,3-trichloropropene-1 with sodium and potassium phenoxides, using these phenoxides in excess, and also with equimolar proportions of the reagents; i.e., under the conditions described by Kotlyarevskii and Korbukh [3]. 1,1-Dichloro-3-phenoxypropene-1 and 1,1-dichloro-3-(o-hydroxyphenyl) propene-1 were isolated. The C-substituted phenol obtained under Kotlyarevskii and Korbukh's conditions was proved to be o-(3,3-dichloroallyl)phenol, [and

not p-(1,1-dichlorallyl) phenol, as these authors thought] by hydrolysis with concentrated sulfuric acid. In this case hydrolysis of the dichlorovinyl group was accompanied by sulfonation of the benzene nucleus; in subsequent work, there-fore, the hydrolyzate was diluted with water and desulfonated by heating in sealed glass ampules to 175-180°. Both the C-substituted phenol with the ortho-structure, obtained from 1,1,1-trichloropropene, and that obtained from 1,1,3-tri-chloropropene-1, give the same product — hydrocoumarin, which on hydrolysis gives o-hydroxyhydrocinnamic acid. p-(3,3-Dichloroallyl) phenol gives p-hydroxyhydrocinnamic acid on hydrolysis with sulfuric acid and subsequent de-sulfonation.

All the O-substituted phenols have the structure of 1,1-dichloro-3-phenoxypropene-1, as was proved by oxidation with potassium permanganate in acetone solution to phenoxyacetic acid. Furthermore, hydrolysis of 1,1-dichloro-3-phenoxypropene-1 with subsequent desulfonation gave benzohydropyrone, whereas chlorination of 1,1-dichloro-3-phenoxypropene-1 gave a compound of the composition $Cl_2C_6H_3OCH_2CH=CCl_2$, which on hydrolysis gave a β-(dichlorophenoxy)propionic acid; this also confirms the presence of the $CH_2CH=CCl_2$ group in the original phenoxydichloropropene. It should be noted that identification of o- and p-dichloroallylphenols is facilita-ted by the fact that they have different melting points: The first compound melts at 25°, and the second at 41°. Kotlyarevskii and Korbukh did not obtain crystalline dichloroallylphenols and, apparently, were working with mixtures. Thus a new, detailed investigation of the structure of the products of condensation of phenol with 1,1,1-trichloropropene and 1,1,3-trichloropropene-1 showed that in all cases only compounds containing the $CH_2CH=CCl_2$ grouping are formed; isomeric compounds containing the $-CCl_2-CH=CH_2$ grouping are not formed. In an alkaline medium both O- and C-substituted products are formed in the reaction, substitution in the nucleus taking place mainly in the ortho-position, to some extent in the para-position, and not at all in the meta-position. The same results were obtained with 1,1,1,3-tetrachloropropane, which apparently is first dehydrochlorinated under the influence of the phenoxide, after which the resulting 1,1,3-trichloropropene-1 behaves in the usual manner.

When 1,1,3-trichloropropene-1 is heated with p-chlorophenol there is formed not only a C-condensation product, but also an O-condensation product, namely, 1,1-dichloro-3-(p-chlorophenoxy)propene-1. The same products are obtained, but in different proportions, on condensation of p-chlorophenol with the trichloropropenes indicated above, in an alkaline medium. On chlorination of the resulting compounds, products of the compositions $Cl_2C_6H_2(OH) CH_2OH=CCl_2$ and $Cl_2C_6H_3OCH_2CH=CCl_2$ are formed, which on hydrolysis by concentrated sulfuric acid readily give acids of the probable structure:
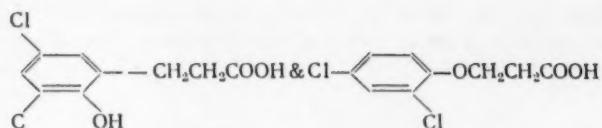
In the present work it is also shown that 1,1-dichloro-3-phenoxypropene-1 isomerizes to 1,1-dichloro-3-(o-hydroxyphenyl)propene-1 on heating with aluminum chloride. Moreover, phenol and a substance having the com-position $C_6H_3(OH) (CH_3CH=CCl_2)_2$, were isolated from the mixture of products; this indicates that the conversion probably proceeds through decomposition according to the scheme

$$C_6H_5O-CH_2CH=CCl_2 \xrightarrow{AlCl_3} C_6H_5OAlCl_2 + ClCH_2CH=CCl_2$$
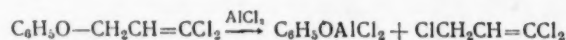
with subsequent alkylation.

EXPERIMENTAL

Condensation of 1,1,3-Trichloropropene-1 with Phenol on Heating (Experiment 1). A mixture of 141 g of phenol (1.5 mole) and 13 g (0.5 mole) of 1,1,3-trichloropropene-1 was heated, with stirring, for 20 min, first at 80-90° and then at 100-110°. The reaction was stopped when 17.2 g of HCl had been evolved. After driving off the unreacted trichloropropene and excess phenol in vacuo there was obtained 93 g of high-boiling products. 1,1-Dichloro-3-(o-hydroxyphenyl)propene-1 was isolated by fractionation in vacuo in a column; b.p. 113-114°(3 mm); n_D^{20} 1.5732; d_4^{20} 1.3056; m.p. 25° (from petroleum ether); yield 61 g (60% of theoretical). Our earlier data [1]: b.p. 116-117° (3 mm); n_D^{20} 1.5727; d_4^{20} 1.3050.

1,1-Dichloro-3-(p-hydroxyphenyl)propene-1 was isolated from the residue through purification of the latter by distillation and then recrystallization from petroleum ether; colorless needles with m.p. 41.5°; yield 19.6 g

(19% of theoretical). Our earlier data [1]: m.p. 41.5°. For proof of the structures of the compounds obtained, see Experiments 4,5, and 6.

Condensation of 1,1,3-Trichloropropene-1 with Phenol in an Alkaline Medium (Experiment 2). a) With the reagents in equimolar proportions. The reactions was performed under the conditions described by Kotlyarevskii and Korbukh [3], with 0.5 mole of 1,1,3-trichloropropene-1. The reaction mixture was acidified with hydrochloric acid and the organic material extracted with heptane, and the heptane solution was then washed three times with 10% NaOH solution. The component insoluble in alkali, which remained in the heptane, was distilled in vacuo, two products being obtained: 1) 1,1-dichloro-3-phenoxypropene-1, b.p. 89-90° (4 mm) n_D^{20} 1.5508; d_4^{20} 1.2596. Found: MR 51.42; $C_9H_8CCl_24F$. Calculated: MR 51.07. Yield 46 g (45% of theoretical). Our earlier data [1]: b.p. 103-104° (7 mm); n_D^{20} 1.5534; d_4^{20} 1.2718*. For proof of the structure of this product, see Experiments 7 and 8.

2) A product of the structure $CCl_2 = CHCH_2C_6H_4OCH_2CH = CCl_2$, with b.p. 137-138° (1 mm); n_D^{20} 1.5670; d_4^{20} 1.3611; found MR 74.89 $C_{12}H_{10}OCl_45F$. Calculated MR 74.19. Found: C 46.45; 46.09; H 3.16; 3.15; Cl 45.47; 45.16%. Calculated: C 46.19; H 3.23; Cl 45.46%.

When the product, which separated on acidification of the alkaline extracts, was distilled in a column in a current of nitrogen, there was obtained only 1,1-dichloro-3-(o-hydroxyphenyl)propene-1, b.p. 94-95° (1.5 mm) 103-104° (2.5 mm), 114-115° (3 mm), 135-136° (6 mm); n_D^{20} 1.5732; d_4^{20} 1.3059. Found MR 51.16. $C_9H_8O_2Cl_24F$. Calculated MR 50.95. Yield 22 g (21% of theoretical). The substance crystallized on cooling. After recrystalliza- tion from petroleum ether, m.p. 25-25.5°. The melting point of a mixed sample of this substance with o-(3,3-di- chloroallyl)phenol prepared as indicated above in Experiment 1, also was 25-25.5°. Besides, 3 g of a residue was obtained, which was not further investigated.

b) With an excess of phenoxide. To a solution of 94 g of phenol and 56 g of KOH in 40 g of H_2O, 73 g of 1,1,3-trichloropropene-1 was added during 15 min, with stirring. Heat was evolved in the reaction; the mixture temperature was kept at 80-90°. When the spontaneous heating ceased, the reaction mixture was heated for 20 min more at this temperature. The reaction mixture was cooled, acidified,and extracted three times with chloro- form. After driving off the chloroform and excess phenol, the residue was distilled in vacuo in the range 60-155° (1 mm). When the distillate was redistilled in a column in a current of nitrogen, there were obtained: 1) 1,1-dichloro- 3-phenoxypropene-1, b.p. 110-111°(7 mm) n_D^{20} 1.5508, d_4^{20} 1.2598; found MR 51.41; calculated MR 51.07. Yield 71 g (70% of theoretical); 2) 1,1-dichloro-3-(o-hydroxyphenyl)propene-1, b.p. 91-92° (1 mm), 141-142° (7 mm), n_D^{20} 1.5733; d_4^{20} 1.3060, m.p. 25°.The melting point of a mixed sample of this substance with a sample of o-(3,3-di- chloroallyl)phenol, prepared as described in Experiment 1, also was 25°. Yield 16.3g (16% of theoretical). Besides 3 g of a product with b.p. 137-138° (1 mm) was isolated, which apparently was $CCl_2 = CHCH_2C_6H_4OCH_2CH = CCl_2$.

Condensation of 1,1,1-Trichloropropene with Phenol in an Alkaline Medium (Experiment 3). a) With the reagents in equimolar proportions. The reaction was carried out under the conditions described by Kotlyarevskii and Korbukh [3]. When the condensation products obtained from 0.5 mole of 1,1,1-trichloropropene, were distil- led in a column in a current of nitrogen, there were isolated: 1) 1,1-dichloro-3-phenoxypropene-1, b.p. 68-69° (1 mm), n_D^{20} 1.5510; d_4^{20} 1.2600; yield 13 g (13% of theoretical); 2) 1,1-dichloro-3-(o-hydroxyphenyl)propene-1, b.p. 90-91° (1 mm), n_D^{20} 1.5735; d_4^{20} 1.3062; m.p. 25-25.5° (from petroleum ether). Yield 31 g (30% of theoretical). The melting point of a mixed sample of this substance with a sample of o-(3,3-dichloroallyl)phenol, prepared as described in Experiment 1, also was 25-25.5°. Besides, 29 g of residue was obtained.

b) With an excess of phenoxide. The experiment was performed in exactly the same way as in the case of 1,1,3-trichloropropene-1. When the condensation products, obtained from 0.5 mole of 1,1,1-trichloropropene, were distilled in a column in a current of nitrogen, there were isolated: 1) 1,1-dichloro-3-phenoxy propene-1, b.p. 68-69° (1 mm), n_D^{20} 1.5510; d_4^{20} 1.2594; yield 69 g (68% of theoretical); 2) 1,1-dichloro-3-(o-hydroxyphenyl) propene-1, b.p. 90-91° (1 mm), n_D^{20} 1.5730; d_4^{20} 1.3058, m.p. 25-25.5°; yield 15 g (15% of theoretical). The melt- ing point of a mixed sample of this substance with o-(3,3-dichloroallyl)phenol prepared as described in Experi- ment 1, also was 25-25.5°. Besides, 12 g of a high-boiling residue was obtained, which was not further investigated.

Preparation of ortho-Hydroxyhydrocinnamic Acid from o-$HOC_6H_4CH_2CH = CCl_2$ (Experiment 4). Six g (0.03 mole) of 1,1-dichloro-3-(o-hydroxyphenyl)-propene-1, prepared as described in Experiments 1-3, was hydrolyzed

*It was found that separation of 1,1-dichloro-3-phenoxypropene-1 from dichloroallylphenol by treating the reac- tion products with alkali, does not give a pure ether. In the present work the product, after treatment with alkali, was fractionated in a column, as a result of which a purer product was obtained.

by heating (80-90°) with 30 g of concentrated sulfuric acid, with vigorous stirring, until hydrogen chloride ceased to be evolved. The hydrolysis was accompanied by sulfonation of the nucleus; therefore the homogeneous solution obtained was diluted with twice its weight of water, sealed into a glass ampule, and heated for 2 hours at 175-180° in a Carius furnace for the purpose of desulfonation. The oil which separated as a result of desulfonation, was extracted with chloroform, the chloroform driven off, and the residue distilled in vacuo. There was obtained a substance, insoluble in cold alkali, with b.p. 125-126° (6 mm), n_D^{20} 1.5570; d_4^{20} 1.1982; yield 3 g (70% of theoret-

ical). Found MR 39.81   calculated MR 39.62. When the resulting substance was dissolved in warm
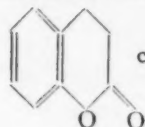
alkali and then acidified with concentrated hydrochloric acid, large, colorless acicular crystals separated out on cooling of the solution. After recrystallization, m.p. 87-87.5°. Literature data for 2-hydroxyhydrocinnamic acid [4]: m.p. 83-84°. Found: C 65.11; 65.13; H 5.97; 5.94%. $C_9H_{10}O_3$. Calculated: C 65.05; H 6.06%. The same results were obtained in the case of 1,1-dichloro-3-(o-hydroxyphenyl)propene-1 prepared under Kotlyarevskii and Korbukh's conditions, as described in Experiment 3.

Chlorination of 1,1-Dichloro-3-(o-hydroxyphenyl)propene-1 (Experiment 5). A solution of 40.6 g (0.2 mole) of 1,1-dichloro-3-(o-hydroxyphenyl)propene-1, b.p. 113-114° (3 mm), n_D^{20} 1.5732; d_4^{20} 1.3056, and m.p. 25°, in 80 g of carbon tetrachloride, was chlorinated at 22-27° for 90 min, until hydrogen chloride ceased to be evolved. On distillation of the reaction products a fraction with b.p. 145-150° (3 mm) was isolated. Yield 37 g; besides, there was obtained 16 g of a residue which did not distil. The volatile fraction was stirred for 1 hour with concentrated H_2SO_4 in order to eliminate all impurities that could be sulfonated, and then was washed and redistilled. There was obtained a colorless substance with b.p. 129-130° (1.5 mm), n_D^{20} 1.5890; d_4^{20} 1.4920. Yield 35 g (64% of theoretical).

When 27.1 g (0.1 mole) of this product was hydrolyzed with 98% sulfuric acid at 70-100° until hydrogen chloride ceased to be evolved, subsequent treatment of the hydrolyzate gave 25.5 g of the crude acid. After recrystallization from heptane, and then hot water, colorless crystals with m.p. 122° were obtained. Literature data for 3,5-dichloro-2-hydroxyhydrocinnamic acid [5]: m.p. 122° (from H_2O). Found: C 46.44; 46.28; H 3.55; 3.56; Cl 30.45; 30.16%; $C_9H_8O_3Cl_2$. Calculated: C 45.99; H 3.43; Cl 30.17%.

Preparation of 4-Hydroxyhydrocinnamic Acid from p-$HOC_6H_4CH_2CH=CCl_2$ (Experiment 6). A 10.2 g quantity (0.05 mole) of 1,1-dichloro-3-(p-hydroxyphenyl)propene-1, m.p. 41°, was hydrolyzed by heating with 40 g of H_2SO_4 (96%) at 40-45° until hydrogen chloride ceased to be evolved; on cooling of the hydrolyzate, the crystalline sulfonic acid was obtained. Yield of crude acid, 14 g. Part of the sulfonic acid (8 g) was dissolved in 100 ml of dilute hydrochloric acid (1:1) and desulfonated in a glass ampule by heating to 175° for 2 hours. On cooling of the resulting homogeneous solution, p-hydroxyhydrocinnamic acid separated out in the form of shiny lamellae. Yield 4.7 g (87% of theoretical). After recrystallization from water, m.p. 128°. Literature data for p-hydroxyhydrocinnamic acid [6]: m.p. 128-129°. Found: C 64.65; 64.56; H 6.03; 5.98%. $C_9H_{10}O_3$. Calculated: C 64.90; H 6.04%.

Oxidation of 1,1-Dichloro-3-phenoxypropene-1 (Experiment 7). To a solution of 20.3 g of $C_6H_5OCH_2CH=CCl_2$, b.p. 68-69° (1 mm), n_D^{20} 1.5510; d_4^{20} 1.2600 in 400 ml of acetone, $KMnO_4$ was added in small portions, and the mixture was stirred at room temperature. The addition of $KMnO_4$ was stopped when the solution ceased to become decolorized. The MnO_2 precipitate was filtered out, washed three times with hot acetone, and then treated several times with boiling water. The combined water extracts were concentrated to 50-75 ml and acidified with hydrochloric acid. The crystalline phenoxyacetic acid which separated was filtered out, dried and recrystallized from heptane; m.p. 99°; yield 7.9 g (52% of theoretical). Literature data for phenoxyacetic acid [7]: m.p. 98-99°. Found: C 63.15; 63.37; H 5.30; 5.31%. $C_8H_8O_3$. Calculated: C 63.15; H 5.30%.
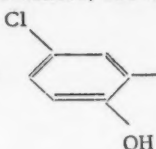
Chlorination of 1,1-Dichloro-3-phenoxypropene-1 (Experiment 8). A solution of 40.7 g (0.2 mole) of $C_6H_5OCH_2CH=CCl_2$ in 80 g of CCl_4 was saturated by a current of chlorine at 40° for 45 min, until 9 g of hydrogen chloride had been evolved. After driving off the solvent, the residue was distilled from a Favorskii flask. Two fractions were obtained. Fr. I had b.p. 107-108° (1.5 mm), n_D^{20} 1.5650; d_4^{20} 1.3756; yield 30 g. The substance partially crystallized on cooling. The separated crystals had m.p. 29° (from petroleum ether), and a mixture test with a known sample of p-$ClC_6H_5OCH_2CH=CCl_2$, prepared as described in Experiments 9 and 10, showed no melting-point depression. The substance was easily hydrolyzed by sulfuric acid; in this case, however, it was completely sulfonated.

Fr. II had b.p. 121-122° (1 mm), n_D^{20} 1.5760; d_4^{20} 1.4650; yield 16 g. Found: C 39.75; 39.90; H 2.27; 2.30% $Cl_2C_6H_3OCH_2CH=CCl_2$. Calculated: C 39.74; H 2.22%. On hydrolysis of 16 g of this substance with sulfuric acid, 10 g of crude, crystalline product was obtained; after elimination of neutral impurities by means of soda solution, followed by recrystallization from hot water, activated charcoal being used for purification, the product had m.p. 118-119.5°, yield 9.4 g. Found: C 45.97; 45.76; H 3.51; 3.57; Cl 29.43; 30.02%. $C_9H_8O_3Cl_2$. Calculated: C 45.99; H 3.43; Cl 30.17%.

Condensation of 1,1,3-Trichloropropene-1 with p-Chlorophenol on Heating (Experiment 9). A mixture of 128 g (1 mole) of p-chlorophenol and 73 g (0.5 mole) of 1,1,3-trichloropropene-1 was heated to boiling and the beginning of hydrogen chloride evolution (145°), after which heating was continued for 1.5 hours more. The reaction was stopped when 12.2 g of HCl had been evolved and the mixture temperature had risen to 180°. After driving off the unreacted trichloropropene and excess p-chlorophenol, the residue was treated with 5% KOH solution and the alkali-insoluble part extracted with heptane. The heptane was driven off and the residue distilled in vacuo. There was obtained 3-(p-chlorophenoxy)-1,1-dichloropropene-1, b.p. 101-102° (1 mm), n_D^{20} 1.5642; d_4^{20} 1.3716. Found MR 56.59. $C_8H_7OCl_34F$. Calculated MR 55.94; m.p. 29-29.5° (from heptane). Yield 17 g (21% of theoretical, reckoned on reacted trichloropropene). Found: C 45.49; 45.73; H 2.94; 2.88; Cl 44.63; 44.41%. Calculated: 45.52; H 2.97; Cl 44.78%.

The alkaline extract was acidified, and the oil which separated was distilled in vacuo; a phenolic product,

apparently having the structure ⟨structure: benzene ring with Cl and OH substituents⟩ —$CH_2CH=CCl_2$, was obtained; b.p. 136-137° (3 mm), 120-121° (1

mm), n_D^{20} 1.5810; d_4^{20} 1.4105. Found MR 56.11. $C_9H_7OCl_34F$. Calculated MR 55.82. Yield 38 g (48% of theoretical). Found: C 45.67; 45.82; H 2.87, 3.01%. Calculated: C 45.52; H 2.97%. Besides, 11 g of a high-boiling residue was obtained, which was not further investigated.

Condensation of 1,1,3-Trichloropropene-1 with Sodium p-Chlorophenoxide (Experiment 10). The reaction between 73 g (0.5 mole) of $ClCH_2CH=CCl_2$ and 102 g (0.8 mole) of $p-ClC_6H_4OH$ in a solution of 32 g (0.8 mole) of NaOH in 25 ml of H_2O was carried out just as described for the case of phenol in Experiment 2.

The reaction mixture was cooled, acidified with dilute hydrochloric acid, and extracted with chloroform. After distilling off the solvent and excess p-chlorophenol, two products were obtained. The first was 1,1-dichloro-3-(p-chlorophenoxy)propene-1, b.p. 101-102° (1 mm), n_D^{20} 1.5650; d_4^{20} 1.3720; m.p. 29°; yield 49 g (41% of theoretical). This substance was insoluble in dilute alkali; treatment with concentrated H_2SO_4 resulted in hydrolysis with evolution of hydrogen chloride, together with sulfonation in the nucleus. The second product had b.p. 120-121° (1 mm), n_D^{20} 1.5815; d_4^{20} 1.4108. This compound was identical in its constants with the substance of the same composition, described in the preceding experiment, and apparently was 1,1-dichloro-3-(5-chloro-2-hydroxyphenyl)-propene-1. Yield 25 g (21% of theoretical). The substance was soluble in dilute alkali, and also was hydrolyzed on treatment with concentrated H_2SO_4, sulfonation and HCl evolution taking place at the same time. Besides, 26 g of a high-boiling residue containing products of a higher degree of alkylation, was obtained.

Condensation of 1,1,1,3-Tetrachloropropane with Phenol in an Alkaline Medium (Experiment 11). A mixture of 188 g (2 moles) of phenol, 112 g (2 moles) of KOH, 80 ml of H_2O, and 182 g (1 mole) of tetrachloropropane was heated, with stirring, at 95-100° for 1 hour. The precipitated KCl was filtered out, and washed with acetone (73 g of KCl was obtained), and the mother liquor was treated with dilute hydrochloric acid and extracted with chloroform. After driving off the chloroform, the unreacted tetrachloropropane (72 g) was steam distilled from the residue. The resulting heavy oil was freed from excess phenol and then distilled; 66 g of a fraction with b.r. 60-150° (1 mm) and 29 g of a nonvolatile residue were obtained. Redistillation of the volatile fraction in a column in a current of nitrogen gave two main products: 1,1-dichloro-3-phenoxypropene-1, b.p. 68-69° (1 mm), n_D^{20} 1.5500; d_4^{20} 1.2603; yield 28 g, and 1,1-dichloro-3-(o-hydroxyphenyl)propene-1, b.p. 90-91° (1 mm), n_D^{20} 1.5740; d_4^{20} 1.3031; m.p. 25° (from petroleum ether). A mixture test with a previously-prepared sample of 1,1-dichloro-3-(o-hydroxyphenyl)propene-1 gave no melting-point depression; yield 31 g.

Isomerization of 1,1-Dichloro-3-phenoxypropene-1 on Treatment with Aluminum Chloride (Experiment 12). A mixture of 51 g (0.25 mole) of $C_6H_5OCH_2CH=CCl_2$, 30 g of n-heptane, and 3 g of aluminum chloride was heated

at 80°, with stirring, for 30 min. After treating the reaction mixture with dilute hydrochloric acid and extracting the oil with heptane, the extracts were dried, the heptane driven off, and the residue distilled in a column. There were obtained phenol, a little of the original phenoxy derivative, and 3-(o-hydroxyphenyl)-1,1-dichloropropene-1, b.p. 90-91° (1 mm), n_D^{20} 1.5736; d_4^{20} 1.3070 and m.p. 25°; yield 30 g. Besides, a high-boiling product was obtained, which was completely soluble in alkali (7 g).

SUMMARY

1. In the condensation of 1,1,1-trichloropropene or 1,1,3-trichloropropene-1 with sodium phenoxide or potassium phenoxide, alkylation takes place both on oxygen and carbon, products of the structures $C_6H_5OCH_2CH = CCl_2$ and $o-HOC_6H_4CH_2CH = CCl_2$ being formed. Compounds containing the grouping $-CCl_2-CH = CH_2$ are not formed.

2. The condensation of these trichloropropenes with phenol gives o- and p-(3,3-dichloroallyl)phenols.

3. The interaction of 1,1,3-trichloropropene-1 with p-chlorophenol or sodium p-chlorophenoxide leads to products of alkylation of oxygen and on carbon, having the compositions $p-ClC_6H_4OCH_2CH = CCl_2$ and $ClC_6H_3(OH)CH_2CH = CCl_2$.

4. 1,1-Dichloro-3-phenoxypropene-1 isomerizes to o-(3,3-dichloroallyl)phenol in the presence of $AlCl_3$.

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SYNTHESIS OF 5,5-DICHLORO-2,4-PENTADIENAL AND SOME OF ITS TRANSFORMATIONS

L. I. Zakharkin and L. P. Sorokina

Institute of Heteroorganic Compounds, Academy of Sciences, USSR

By condensation of β,β-dichloroacrolein with carbonyl compounds we previously [1] obtained a series of dichlorodienic ketones with the structure $RCOCR' = CH - CH = CCl_2$. 5,5-Dichloro-2,4-pentadienal, $CCl_2 = CH - CH$ $=CH - CHO$, the vinylog of β,β-dichloroacrolein could not be synthesized by this method. In the present work we found that 5,5-dichloro-2,4-pentadienal is obtained in high yield by the following route:

$$CCl_2 = CH — CHClOC_2H_5 + CH_2 = CHOC_2H_5 \xrightarrow{ZnCl_2}$$

$$\rightarrow CCl_2 = CH — \overset{\overset{\displaystyle OC_2H_5}{|}}{CH} — CH_2CHClOC_2H_5 \xrightarrow[H+]{H_2O} CCl_2 = CH — CH = CH — CHO$$
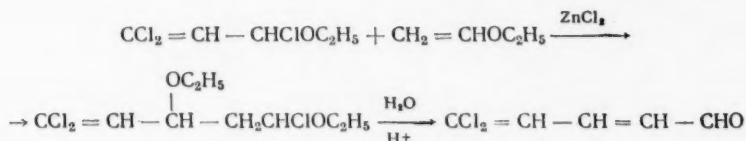
Condensation of the easily accessible 1,1,3-trichloro-3-ethoxy-1-propene [2] with ethyl vinyl ether in presence of a small quantity of zinc chloride at temperatures below zero gives 1,1,5-trichloro-3,5-diethoxy-1-pentene in high yield. Without separation from the reaction medium, the latter is subjected to hydrolysis with dilute hydrochloric acid and the resulting dichloropentadienal is distilled with steam at the same time. Condensation of β,β-dichloroacrolein diethylacetal with ethyl vinyl ether in presence of zinc chloride leads to 1,1-dichloro-3,5,5-triethoxy-1-pentene. In this case the yield is lower than for 1,1,3-trichloro-3-ethoxy-1-propene. Hydrolysis of 1,1-dichloro-3,5,5-triethoxy-1-pentene with dilute hydrochloric acid gives the dichloropentadienal in good yield:

$$CCl_2 = CH — CH (OC_2H_5)_2 + CH_2 = CHOC_2H_5 \xrightarrow{ZnCl_2}$$

$$\rightarrow CCl_2 = CH — CH (OC_2H_5) CH_2CH (OC_2H_5)_2 \xrightarrow[H+]{H_2O} CCl_2 = CH — CH = CH — CHO$$
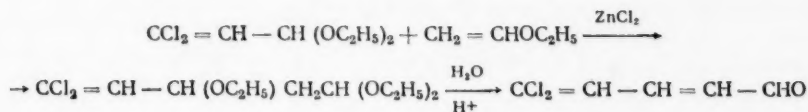
An attempt was also made to prepare dichloropentadienal by another route. Carbon tetrachloride reacts with vinyl acetate in presence of benzoyl peroxide to give, according to the patent literature [3], a mixture of telomers with the structure $CCl_3(CH_2CHOCOCH_3)_nCl$. When this reaction was carried out in presence of azodiisobutyronitile and with a 4:1 molar ratio of CCl_4: to vinyl acetate, the main products were found to be telomers with $n = 1$ and 2. Hydrolysis of 1,1,1,5-tetrachloro-3,5-diacetoxypentane with hydrochloric acid and distillation with steam gives 5,5,5-trichloro-2-pentenal in admixture with dichloropentadienal.

$$CCl_3CH_2CH (OCOCH_3) CH_2CHClOCOCH_3 \xrightarrow[H+]{H_2O}$$

$$\rightarrow CCl_3CH_2CH = CH — CHO + CCl_2 = CH — CH = CH — CHO$$
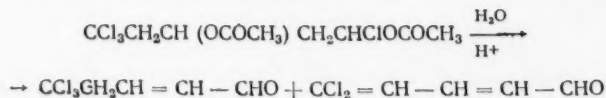
Under these conditions 1,1,1,3-tetrachloro-3-acetoxypropane is entirely converted into β,β-dichloroacrolein.

2,4-Dinitrophenylhydrazine acts on tetrachlorodiacetoxypentane in an acid medium to form 5,5,5-trichloro-2-pentenal. 5,5-Dichloro-2,4-pentadienal is a light-yellow liquid, easily oxidized in the air to 5,5-dichloro-2,4-pentadienic acid

$$CCl_2 = CH - CH = CH - CHO \xrightarrow{O_2} CCl_2 = CH - CH = CH - COOH$$
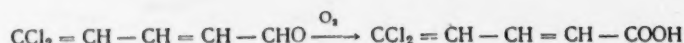
In carbon tetrachloride one molecule of bromine smoothly adds on to dichloropentadienal. The resulting 2,3-dibromo-5,5-dichloro-4-pentenal loses hydrogen bromide on standing to form the crystalline 2-bromo-5,5-dichloro-1,4-pentadienal

$$CCl_2 = CH - CH = CH - CHO + Br_2 \rightarrow CCl_2 = CH - CHBr - CHBrCHO \rightarrow$$
$$\rightarrow CCl_2 = CH - CH = CBr - CHO$$
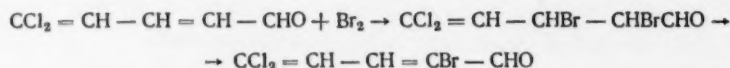
Dichloropentadienal readily condenses with acetophenone in presence of hydrogen chloride to give the corresponding trienic ketone

$$C_6H_5COCH_3 + CCl_2 = CH - CH = CH - CHO \xrightarrow{H+}$$
$$\rightarrow C_6H_5COCH = CH - CH = CH - CH = CCl_2$$
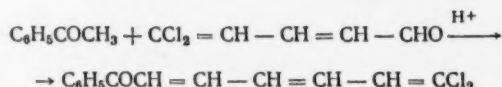
Heating of dichloropentadienal in acetic acid solution leads to α-pyrone

$$CCl_2 = CH - CH = CH - CHO \xrightarrow{CH_3COOH}$$
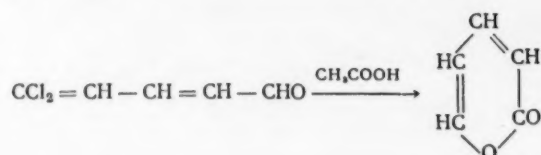
Dichloropentadienal can be employed for synthesis of dienic acids according to the following scheme:

$$CCl_2 = CH - CH = CH - CHO + RMgX \rightarrow RCH (OH) CH = CH - CH = CCl_2 \rightarrow$$
$$\rightarrow RCH = CH - CH = CH - COOH$$
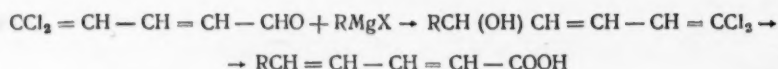
When R = Ar the conversion of the dichlorodienic alcohol to the corresponding dienic acid takes place, as we showed earlier [4], under the action of acids due to an anionic allyl rearrangement. When R = alkyl the dichlorodienic alcohol does not undergo the anionic allyl rearrangement but splits off water to give the dichlorotriene. Heating of 1,1-dichloro-5-hydroxy-1,3-heptadiene in aqueous dioxanic solution in presence of sulfuric acid thus gave only 1,1-dichloro-1,3,5-heptatriene

$$CCl_2 = CH - CH = CH - CHO + C_2H_5MgBr \rightarrow C_2H_5CH (OH) CH = CH - CH = CCl_2 \xrightarrow{H+}$$
$$\rightarrow CH_3CH = CH - CH = CH - CH = CCl_2$$
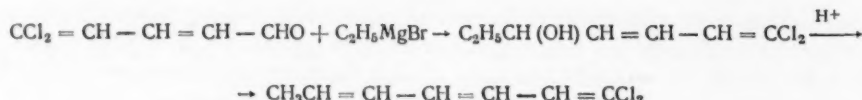
When R = alkyl the conversion to the dienic acid is effected by alkaline hydrolysis of the dichlorovinyl group with simultaneous removal of water. In this way the heating of 1,1-dichloro-5-hydroxy-1,3-octadiene with potassium hydroxide solution in diethyleneglycol gives 2,4-octadienic acid

$$CCl_2 = CH - CH = CH-CHO + C_3H_7MgBr \rightarrow C_3H_7CH (OH) CH = CH - CH = CCl_2 \xrightarrow[H_2O]{KOH}$$
$$\rightarrow C_3H_7CH = CH - CH = CH - COOH$$
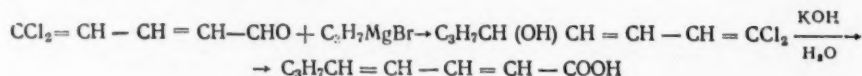
Reaction of hexynemagnesium bromide with dichloropentadienal gave the acetylenic alcohol. On heating in aqueous dioxanic solution in presence of sulfuric acid, this alcohol undergoes both the anionotropic allylic rearrangement with formation of acetylenedienic acid and rearrangement to the dichlorotrienic ketone:

$$C_4H_9C \equiv CMgBr + CCl_2 = CH - CH = CH - CHO \rightarrow C_4H_9C \equiv C - CH (OH) CH =$$

$$= CH - CH = CCl_2 \xrightarrow{H^+} C_4H_9COCH = CH - CH = CH - CH = CCl_2 + C_4H_9C \equiv$$

$$\equiv C - CH = CH - CH = CH - COOH$$
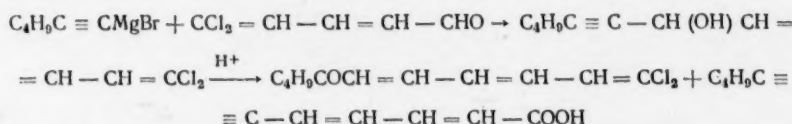
The ketone is formed in larger quantity than the acid.

Dichloropentadienal is prepared by cleavage of a molecule of alcohol from 1,1-dichloro-3,5,5-triethoxy-1-pentene on heating with $KHSO_4$. Heating with potassium hydroxide results in loss of hydrogen chloride with formation of the chloroacetyl compound

$$CCl_2 = CH - \overset{\overset{\displaystyle OC_2H_5}{|}}{CH} - CH_2 - CH (OC_2H_5)_2 \xrightarrow{KHSO_4} CCl_2 = CH -$$

$$- CH = CH - CH (OC_2H_5)_2 \xrightarrow{KOH} ClC \equiv C - CH = CH - CH (OC_2H_5)_2.$$
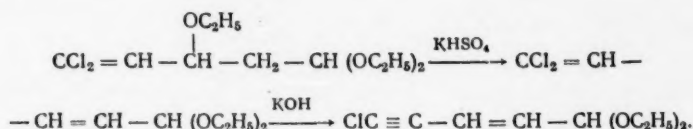
Treatment of 1,1-dichloro-3,5,5-triethoxy-1-pentene with sodium, followed by decomposition of the reaction product with water, gives 1,1,3-triethoxy-4-pentyne in high yield

$$CCl_2 = CH - \overset{\overset{\displaystyle OC_2H_5}{|}}{CH} - CH_2CH (OC_2H_5)_2 \xrightarrow[H_2O]{Na} HC \equiv C - \overset{\overset{\displaystyle OC_2H_5}{|}}{CH} - CH_2 - CH (OC_2H_5)_2$$
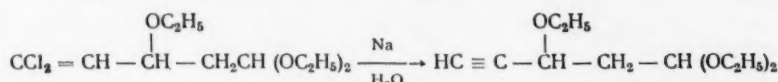
EXPERIMENTAL

1,1,5-Trichloro-3,5-diethoxy-1-pentene. At a temperature of -5 to 3°, 20 g of vinyl ethyl ether was gradually stirred into 50 g of 1,1,3-trichloro-3-ethoxy-1-propene to which a solution of 0.3 g of zinc chloride in 2 g of ethyl acetate had been added. The solution was then allowed to stand for half an hour. After addition of 2 g of finely pulverized, calcined potassium carbonate, the mixture was stirred for 20 min. The precipitate was filtered, and the filtrate distilled in vacuo. Yield 62.2 g of 1,1,5-trichloro-3,5-diethoxy-1-pentene with b.p. 85-86° (2 mm); n_D^{20} 1.4672, d_4^{20} 1.1677. Found C 41.58; 41.60; H 5.89; 5.84%. $C_9H_{15}Cl_3O_2$. Calculated: C 41.30; H 5.73%.

1,1-Dichloro-3,5,5-triethoxy-1-pentene. Into 59 g of 1,1-dichloro-3,3-diethoxy-1-propene and 8.5 ml of 10% solution of zinc chloride in ethyl acetate was gradually stirred 27 g of vinyl ethyl ether at such a rate that the temperature did not rise above 45°. After addition of the whole of the vinyl ethyl ether, the reaction mixture was stirred for an hour at 45° and 1.5 hr at 50-60°. The cooled reaction mixture was diluted with an equal volume of ether, washed with 5% sodium hydroxide solution, and dried over potassium carbonate. Distillation in vacuo gave 20.3 g of the original dichlorodiethoxypropene and 37.2 g (70.5% of theory on the reacted dichlorodiethoxypropene) of 1,1-dichloro-3,5,5-triethoxy-1-pentene with b.p. 96-98° (2 mm); n_D^{20} 1.4480; d_4^{20} 1.0752; Found: MR 67.49; calculated MR 67.20. Found: C 48.78; 48.76; H 7.31; 7.31%. $C_{11}H_{20}Cl_2O_3$. Calculated: C 48.70; H 7.38%.

5,5-Dichloro-2,4-pentadienal. To the product of reaction of 50 g of trichloroethoxypropene with 19 g of vinyl ethyl ether was added 20 ml of concentrated hydrochloric acid and 20 ml of water, and the mixture was distilled with steam. The oil in the distillate was extracted with chloroform and dried over calcium chloride. Yield 30 g (67.8% of the theoretical) of 5,5-dichloro-2,4-pentadienal with b.p. 76-77° (8 mm); n_D^{20} 1.5949; d_4^{20} 1.3124. Found: C 39.77; 39.58; H 2.84; 2.78%. $C_5H_4Cl_2O$. Calculated: C 39.73; H 2.64%

The 2,4-dinitrophenylhydrazone had m.p. 174-175° (from the acetic acid). Found: N 16.98; 17.06%. $C_{11}H_8Cl_2N_4O_4$. Calculated: N 16.98%. The semicarbazone had m.p. 189-190° (from alcohol). Found: N 20.02; 19.84%. $C_6H_7Cl_2N_3O$. Calculated: N 20.18%.

To 20 g of 1,1-dichloro-3,5,5-triethoxypentene was added 15 ml of concentrated hydrochloric acid and 10 ml of water, and the mixture distilled with steam. The oil in the distillate was extracted with chloroform. Distillation gave 8.1 g (78% of the theoretical) of 5,5-dichloropentadienal with b.p. 76-77° (8 mm); n_D^{20} 1.5945.

1,1,1,5-Tetrachloro-3,5-diacetoxypentane. To 450 g of dry carbon tetrachloride and 0.5 g of azodiisobutyronitrile was added, in the course of an hour at 75-76°, 120 g of vinyl acetate containing 0.5 g of azodiisobutyronitrile. The solution was then boiled for 2.5 hr. Excess of carbon tetrachloride was taken off in vacuo and the residue distilled. Yield 60.3 g of 1,1,1,3-tetrachloro-3-acetoxypropane and 121 g of 1,1,1,5-tetrachloro-3,5-diacetoxypentane with b.p. 123-125° (2 mm); n_D^{20} 1.4770; d_4^{20} 1.3814; Found MR 66.68; calculated MR 66.84. Found: C 33.13; 33.23; H 3.73; 3.73%. $C_9H_{12}Cl_4O_4$. Calculated: C 32.92; H 3.66%.

Treatment with 2,4-dinitrophenylhydrazine in an alcoholic medium in presence of sulfuric acid gave the 2,4-dinitrophenylhydrazone of 5,5,5-trichloropenten-2-al with m.p. 147-148° (from acetic acid). Found: N 15.52; 15.31%. $C_{11}H_9Cl_3N_4O_4$. Calculated N 15.24%.

Hydrolysis of 1,1,1,5-tetrachloro-3,5-diacetoxypropane (from an experiment with 200 g of vinyl acetate). 75 ml of concentrated hydrochloric acid and 35 ml of water were added to the residue (250 g), and the mixture was distilled with steam. The distillate was extracted with chloroform. The extract was dried over calcium chloride, the solvent removed, and the residue distilled in vacuo. There was obtained 61.2 g of a mixture of 5,5,5-trichloropenten-2-al and dichloropentadienal with b.p. 78-80° (8 mm); n_D^{20} 1.5742; d_4^{20} 1.3278. Found: C 37.31; H 2.66; Cl 50.02%.

Treatment of the mixture with 2,4-dinitrophenylhydrazine gave the hydrazone of dichloropentadienal with m.p. 174-175°. Hydrolysis under similar conditions of 150 g of 1,1,1,3-tetrachloro-3-acetoxypropane gave 61 g (78% of theory) of β,β-dichloroacrolein with b.p. 125-126°; n_D^{20} 1.5080. Literature data [5]: b.p. 124-125°; n_D^{20} 1.5090.

5,5-Dichloro-2,4-pentadienic acid. The acid was obtained (yield 24% of theory) when dichloropentadienal was left to stand in the air. M.p. 120-122° (from ligroine). A mixture with the acid obtained by oxidation of dichloropentadienal with moist silver oxide melted at 120-122°. Found: C 36.16; 36.28; H 2.43; 2.55%. $C_5H_4Cl_2O_2$. Calculated: C 35.92; H 2.39%.

2,3-Dibromo-5,5-dichloropenten-4-al. To a solution of 44 g of dichloropentadienal in 100 ml of carbon tetrachloride was slowly added 45 g of bromine at 5-10°. The solvent was removed in vacuo, and the residue distilled in vacuo. Yield 86.3 g of 2,3-dibromo-5,5-dichloropenten-4-al with b.p. 90-91° (1 mm); n_D^{20} 1.5823; d_4^{20} 2.0135. Found: C 19.74; 19.64; H 1.33; 1.30%. $C_5H_4Br_2Cl_2O$. Calculated: C 19.30; H 1.28%.

The product easily splits off hydrogen bromide on standing and gives 2-bromo-5,5-dichloropentienal; m.p. 97-98° (from alcohol). Found: C 26.53; 26.23; H 1.47; 1.26%. $C_5H_3BrCl_2O$. Calculated: C 26.12; H 1.30%.

2,4-Dinitrophenylhydrazine acts on 2,3-dibromo-5,5-dichloropentenal and 2-bromo-5,5-dichloropentadienal to form the same hydrazone with m.p. 215-216° (from acetic acid). Found: N 13.76; 13.76%. $C_{11}H_4BrClN_4O_4$. Calculated N 13.72%.

α-Pyrone. A solution of 7 g of dichloropentadienal in 15 ml of acetic acid was boiled for 6 hr. Distillation of the acetic acid in vacuo left 1.8 g (38% of theory) of α-pyrone with m.p. 78-80° (7 mm); n_D^{20} 1.5280; d_4^{20} 1.2039. Literature [6]: $d_4^{19.5}$ 1.2006.

Heating of α-pyrone with maleic anhydride gave a crystalline adduct with m.p. 187° (from acetonitrile). Literature data [7]: m.p. of adduct 187°. Found: C 55.64; 55.64; H 3.18; 3.05%. $C_9H_6O_5$. Calculated: C 55.67; H 3.11%.

In addition to the α-pyrone there was obtained 1.5 g of a product with b.p. 124-125° (7 mm); n_D^{20} 1.5080; d_4^{20} 1.2733, which with 2,4-dinitrophenylhydrazine forms a hydrazone with m.p. 174-175°. This did not give a depression in admixture with the 2,4-dinitrophenylhydrazone of 5,5-dichloropentadienal.

1,1-Dichloro-7-phenyl-1,3,5-heptatrien-6-one. A mixture of 10 g of dichloropentadienal and 8 g of acetophenone was saturated with dry hydrogen chloride for 20 min while cooling with ice water. The resulting solid product was recrystallized from alcohol; yield 14 g, m.p. 119-120°. Found: C 61.60, 61.71; H 4.04; 4.09%. $C_{13}H_{10}Cl_2O$. Calculated: C 61.65; H 3.95%.

1,1-Dichloro-5-hydroxy-1,3-heptadiene. To ethylmagnesium bromide (from 35 g of ethyl bromide and 8 g of magnesium) in 80 ml of ether was gradually added 38 g of dichloropentadienal. There was obtained 42.1 g of 1,1-dichloro-5-hydroxy-1,3-heptadiene with b.p. 101-102° (3 mm); n_D^{20} 1.5312; d_4^{20} 1.1886. Found C 46.21; 46.18; H 5.34; 5.43%. $C_7H_{10}Cl_2O$. Calculated: C 46.40; H 5.52%.

No acidic reaction products were obtained after heating for four hr of a solution of 10 g of dichlorohydroxyheptadiene in 70 ml of dioxane and 3 ml of water containing 0.5 ml of concentrated sulfuric acid. The sole neutral product of the reaction was 1,1-dichloro-1,3,5-heptatriene with b.p. 74-75° (7 mm); n_D^{20} 1.5766; d_4^{20} 1.1133. Found: C 51.34; 51.41; H 4.82; 4.70%. $C_7H_8Cl_2$. Calculated: C 51.53; H 6.15%.

1,1-Dichloro-5-hydroxy-1,3-octadiene. To propylmagnesium bromide (from 28 g of n-propyl bromide and 3.4 of magnesium) in 60 ml of ether at room temperature was added 26 g of dichloropentadienal in 20 ml of ether. After heating for 15 min, the mixture was cooled and poured into acidified water. There was obtained 26.8 g of 1,1-dichloro-5-hydroxy-1,3-octadiene with b.p. 102-103° (3 mm); n_D^{20} 1.5240; d_4^{20} 1.1547. Found: C 49.34; 49.01; H 5.86; 5.96%. $C_8H_{12}Cl_2O$. Calculated: C 49.23; H 6.15%.

2,4-Octadienic acid. To a stirred solution of 43 g of potassium hydroxide in 86 ml of diethyleneglycol and 8.6 ml of water at 100° was gradually added 26 g of dichlorohydroxyoctadiene. The mixture was then heated at 120-125° for 5 hr. After cooling, water was added and the mixture extracted with ether. The alkaline solution was separated, acidified with hydrochloric acid, and carefully extracted with ether. The ethereal extract was dried over sodium sulfate. There was obtained 8.1 g of a mixture of octadienic acids (liquid and crystalline) with b. r. 130-180° (4 mm). The crystalline acid had m.p. 75.5-76° (from ligroine). Found: C 68.85; 68.66; H 8.31; 8.54%. $C_8H_{12}O_2$. Calculated: C 68.57; H 8.57%.

The liquid acid had b.p. 114-115° (2 mm); n_D^{20} 1.5057; d_4^{20} 0.9767. Found: C 68.35; 68.21; H 8.65; 8.72%. $C_8H_{12}O_2$. Calculated: C 68.57; H 8.57%.

Hydrogenation of the liquid and crystalline octadienic acid gave caprylic acid which was identified through its amide; m.p. 105-106°. A mixture of the amide with an authentic specimen of carylamide melted at 105-106°.

1,1-Dichloro-5-hydroxy-1,2-undecadien-6-yne. To hexynemagnesium bromide (from 14 g of butylacetylene) in 50 ml of ether was gradually added 18 g of dichloropentadienal at the boiling point of ether. After boiling for 3 hr, the solution was cooled and decomposed with acidified water. The ethereal solution was separated and dried over potassium carbonate. There was obtained 20.3 g of 1,1-dichloro-5-hydroxy-1,2-undecadien-6-yne with b.p. 145-146° (3 mm); n_D^{20} 1.5370; d_4^{20} 1.1264. Found: C 56.45; 56.42; H 5.98; 6.00%. $C_{11}H_{14}Cl_2O$. Calculated: C 56.65; H 6.00%.

Isomerization of 1,1-dichloro-5-hydroxy-1,2-undecadien-6-yne. A solution of 14 g of dichloroundecadienyne in 70 ml of dioxane and 4 ml of water was boiled in presence of 0.5 ml of concentrated sulfuric acid for 6 hr. After cooling of the reaction mixture, water was added and the oil extracted with ether. The ethereal solution was washed with 10% potassium hydroxide solution and dried over calcium chloride. The alkaline solution was acidified with hydrochloric acid and extracted with chloroform. Removal of the ether left 10 g of neutral product which crystallized on standing. Melting point of 1,1-dichloro-1,3,5-undecatrien-6-one 58-59° (from ligroine). Found: C 56.44; 56.49; H 6.10; 6.13; Cl 30.26; 30.35%. $C_{11}H_{14}Cl_2O$. Calculated: C 56.65; H 6.00; Cl 30.44%.

2,4-Dinitrophenylhydrazone: m.p. 176-177° (from acetic acid). Found: N 13.23; 13.43%. $C_{17}H_{18}Cl_2N_4O_4$. Calculated: N 13.56%.

Removal of the chloroform left 2.5 g of 2,4-undecadien-6-ynic acid with m.p. 82-83° (from ligroine). Found: C 74.21; 74.09; H 7.80; 7.93%. $C_{11}H_{14}O_2$. Calculated: C 74.15; H 7.86%.

5,5-Dichloro-2,4-pentadienal diethylacetal. A mixture of 56 g of 1,1-dichloro-3,5,5-triethoxy-1-pentene and 0.3 g of potassium bisulfate was heated in a Claisen flask on an oil bath at 130-150°. Ethyl alcohol distilled off during the process. After 9.6 g of alcohol had been collected, the residue was distilled in vacuo to give 34.8 g of dichloropentadienal diethylacetal with b.p. 100-102° (7 mm); n_D^{20} 1.4920; d_4^{20} 1.1208. Found: C 48.15; 48.12; H 6.07; 6.07%. $C_9H_{14}Cl_2O_2$. Calculated: C 48.00; H 6.22%.

5-Chloro-2-penten-4-ynal. A mixture of 30 g of dichloropentadienal diethylacetal and 50 g of potassium hydroxide powder was heated in a Claisen flask at a pressure of 10-20 mm. The dehydrochlorinated product was distilled. Ether was added to the distillate. The ethereal layer was separated from the water and dried over potassium carbonate. Yield 8.9 g of 5-chloro-2-penten-4-ynal with b.p. 89-90° (8 mm); n_D^{20} 1.4742; d_4^{20} 1.0360. Found: C 57.32; 57.48; H 6.92; 6.74; Cl 18.45; 18.53%. $C_9H_{13}ClO_2$. Calculated: C 57.29; H 6.89; Cl 18.83%.

2,4-Dinitrophenylhydrazone: m.p. 178-179° (from acetic acid). Found: N 18.88; 18.86%. $C_{11}H_7ClN_4O_4$ Calculated: N 19.02%.

1,1,3-Triethoxy-4-pentyne. Into 16.5 g of finely pulverized sodium in 100 ml of ether was gradually stirred 47 g of 1,1-dichloro-3,5,5-triethoxypentene at such a rate that the ether boiled gently. After completion of the addition, the mixture was heated for 4 hr, then cooled and carefully decomposed with water. The ethereal solution was dried over potassium carbonate. Yield 25.6 g (78%) of 1,1,3-triethoxypentyne with b.p. 82-83° (8 mm); n_D^{20} 1.4233; d_4^{20} 0.9142. Found: C 65.81; 65.91; H 10.03; 9.83%. $C_{11}H_{20}O_3$. Calculated: C 66.00; H 10.00%.

SUMMARY

1. A convenient method was found for the preparation of 5,5-dichloro-2,4-pentadienal from the product of condensation of β,β-dichloroacrolein diethylacetal with vinyl ethyl ether.

2. Some transformations of 5,5-dichloro-2,4-pentadienal, notably to α-pyrone and dienic acids, were investigated.

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ORGANOBORON COMPOUNDS

COMMUNICATION 58.* THE ACTION OF AMINES AND AMMONIA ON DIARYLCHLOROBORONS

B. M. Mikhailov and N. S. Fedotov

N. A. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSSR
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In preceding investigations we showed that diphenylboron chloride behaves differently towards primary amines than towards secondary amines. With secondary amines the chlorine is replaced by the amino radical at room temperature [2]

$$(C_6H_5)_2BCl + 2R_2NH = (C_6H_5)_2BNR_2 + RNH_3Cl,$$
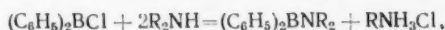
whereas with primary amines complex compounds $(C_6H_5)_2BCl\cdot2\ NH_2R$ with structure (I) are formed, and these are converted into N-alkyl derivatives of diphenylaminoboron only at 200-250° [3]

$$\left[(C_6H_5)_2B\begin{matrix}Cl\\NHR\end{matrix}\right]^-\overset{+}{N}RH_3$$
(I)
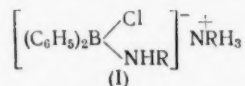
The formation of diamine complexes (I) and their thermal transformations throw light on the mechanism of replacement of the halogen in organoboron halides by alkylamino groups. Reactions between diphenylboron chloride and secondary amines evidently also proceed through the step of formation of corresponding complexes of type (I), but the latter are less stable and break down even at room temperature into N-substituted diphenylaminoborons. The stability of complex (I) is governed not by the electronegativity of the substituted amino groups but by the number and size of the radicals linked to nitrogen. It was found, for instance, that aniline (a primary aromatic amine) reacts with diphenylboron chloride similarly to secondary aliphatic amines with formation at room temperature of diphenylphenylaminoboron

$$(C_6H_5)_2BCl + C_6H_5NH_2 \rightarrow \left[(C_6H_5)_2B\begin{matrix}Cl\\NHC_6H_5\end{matrix}\right][NH_3C_6H_5]^+ \rightarrow$$
$$\rightarrow (C_6H_5)_2B-NHC_6H_5 + C_6H_5NH_2\cdot HCl$$
(II)
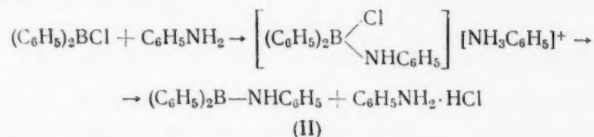
(II). If the stability of complexes (I) depended on the polarity of the substituted amine groups, then the ethylamino radical should have occupied a position intermediate between the diethylamino and phenylamino groups in respect to its influence on the stability of the complexes. In reality, however, it exerts the maximum stabilizing action.

The nature of the aromatic radical at the boron atom also has a marked influence on the reactivity of diarylboron chlorides. It was thus found that di-α-naphthylboron chloride is converted to the corresponding N-substituted di-α-naphthylaminoboron (III) both by primary aliphatic and aromatic amines

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* Communication 57 see [1].

$$(\alpha\text{-}C_{10}H_7)_2BCl + 2RR'NH = (\alpha\text{-}C_{10}H_7)_2BNRR' + RR'NHCl$$

<div align="center">(III)</div>

$$R = CH_3-, \quad C_2H_5-, \quad i\text{-}C_4H_9-, \quad C_6H_5-; \quad R' = H-, C_2H_5-$$
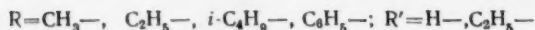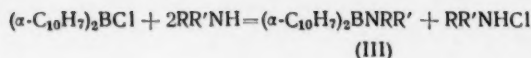
In this manner we prepared di-α-naphthylmethylaminoboron, di-α-naphthylisobutylaminoboron, di-α-naphthyl-phenylaminoboron, and di-α-naphthyldiethylaminoboron.

Diphenylboron chloride and di-α-naphthylboron chloride likewise differ in their behavior towards ammonia. Di-α-naphthylaminoboron (IV) is formed smoothly when ammonia is passed in the cold into a benzene solution of di-α-naphthylboron chloride

$$(\alpha\text{-}C_{10}H_7)_2\,BCl + 2NH_3 = (\alpha\text{-}C_{10}H_7)_2\,BNH_2 + NH_4Cl$$

<div align="center">(IV)</div>
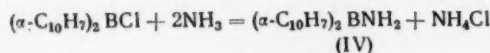
Diphenylboron chloride forms a stable complex compound with ammonia, as we found earlier [2]. This compound was originally assumed to be diphenylboron chloride monoammoniate on the basis of determination of the contents of only boron and chlorine. However, the contents of these elements in the monoammoniate and diammoniate are very similar, and a complete analysis showed it to be the dimmoniate of diphenylboron chloride. Due to its salt-like character, it probably has the heteropolar structure of (V)

$$\left[(C_6H_5)_2\,B\begin{array}{c}Cl\\ \diagdown\\ NH_2\end{array} \right]^{-} \overset{+}{N}H_4$$

<div align="center">(V)</div>
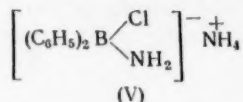
Hydrolysis of complex (V) gives the ammonium salt of diphenylborenic acid (VI)

$$\left[(C_6H_5)_2B\begin{array}{c}Cl\\ \diagdown\\ NH_2\end{array} \right]^{-} \overset{+}{N}H_4 + 2H_2O = [(C_6H_5)_2B\,(OH)_2]^{-} \overset{+}{N}H_4 + NH_4Cl$$

<div align="center">(VI)</div>
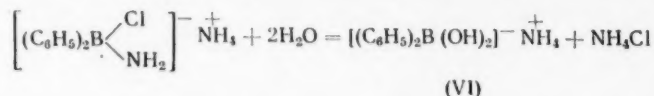
Attempts to thermally convert complex (V) into diphenylaminoboron were unsuccessful. The latter could not be obtained by the action of ammonia on a boiling benzene solution of diphenylboron chloride. Reaction under these conditions gives triphenylboron ammoniate. N-Substituted diphenylaminoborons and di-α-naphthylamino-borons differ in their behavior to water in dependence on the nature of the aromatic radicals linked to the boron and on the character of the radicals at the amino group. Diphenylphenylaminoboron and di-α-naphthylphenyl-aminoboron, for example, are hydrolyzed with facility by moist air, whereas di-α-naphthyldiethylaminoboron remains unchanged after heating with water at 100° for an hour. Di-α-naphthylaminoboron, di-α-naphthylmethyl aminoboron, and di-α-naphthylisobutylaminoboron remain unchanged under the action of water at room temperature for an hour, but are hydrolyzed by water at 100° to form the respective amine and di-α-naphthylboric acid which breaks down under these conditions to naphthalene and α-naphthylboric acid.

The investigated compounds are more resistant to the action of water than hexamethylborazole [4] which is hydrolyzed by water at room temperature. Consequently the relative resistance of borazole and its derivatives to hydrolyzing agents is not a specific characteristic of cyclic compounds with boron—nitrogen bonds, but is also inherent in open-chain nitrogen compounds of boron.

<div align="center">EXPERIMENTAL</div>

Diphenylphenylamino boron. A solution of 9.2 g (0.045 mole) of diphenylboron chloride in 50 ml of absolute ether was placed in a four-necked flask equipped with stirrer, reflux condenser, dropping funnel, and nitrogen inlet tube. A solution of 8.4 g (0.09 mole) of aniline in 50 ml of absolute ether was slowly stirred into the chloride solution. The ether boiled and aniline hydrochloride came down (5.8 g, m.p. 197-199°). The precipitate was filtered the ether distilled off from the ethereal mother liquor, and the residue subjected to fractional distillation. There was obtained 9 g (76.2% of theory) of diphenylphenylaminoboron with b.p. 134-135° (0.04 mm) in the form of a

colorless, viscous oil which crystallized on standing; m.p. 57-59° (in sealed capillary). Found: C 84.10; 84.19; H 6.26; 6.26; B 4.29; 4.40%; M 257.2; 260.7. $C_{18}H_{16}BN$. Calculated: C 84.07; H 6.27; B 4.20%; M 257.1. Diphenylphenylaminoboron is readily soluble in benzene and ether. Very easily hydrolyzed in the air.

Complex of diphenylboron chloride with two molecules of ammonia. A stream of dry ammonia was passed for an hour at 0 to -3° into an isopentane solution (100 ml) of 10 g of diphenylboron chloride. The colorless finely crystalline precipitate was filtered and washed with isopentane. Yield 10.2 g (87.2% of theory) of complex of diphenylboron chloride with two molecules of ammonia. The complex softens at 175-180° and does not melt completely when further heated to 250° (in a sealed capillary). Found: C 59.13; 58.93; H 7.27; 7.43; B 4.60; 4.65; Cl 16.57; 15.77; N 11.70; 11.76%. $C_{12}H_{16}BN_2Cl$. Calculated: C 61.44; H 6.87; B 4.61; Cl 15.13; N 11.93%.

Complex of diphenylboron chloride with triethylamine. A solution of 2.5 g (0.0125 mole) of diphenylboron chloride in 10 ml of n-heptane was put into a funnel for filtration under nitrogen, and 2.5 g (0.025 mole) of triethylamine dissolved in 10 ml of n-heptane was added dropwise in the course of 10 min. Heat was released and a precipitate formed. The latter was filtered and washed with n-heptane. Yield 2.34 g (62.2% of theory) of complex of diphenylboron chloride with triethylamine in the form of colorless needles, quickly turning yellow when kept; m.p. 125-133° (in sealed capillary). Found: B 3.48; Cl 12.04; N 4.80%. $C_{18}H_{25}BNCl$. Calculated: B 3.58; Cl 11.77; N 4.64%.

Action of ammonia on diphenylboron chloride in boiling benzene. A solution of 6.2 g of diphenylboron chloride in 55 ml of absolute benzene was put in a flask fitted with reflux condenser, capped by a calcium chloride tube, and a tube for admission of dry ammonia. Ammonia was passed into the boiling solution for an hour. The benzene was then distilled off from the reaction mass and the residue extracted with boiling ether. The insoluble precipitate was filtered and the solvent distilled. There was obtained 3.83 g (71.7% of theory) of triphenylboron ammoniate which after crystallization from a mixture of benzene and isopentane had m.p. 216-217° in a sealed capillary). No depression in a mixture with triphenylboron ammoniate [5].

Hydrolysis of the diphenylboron chloride—ammonia complex. The complex (3.13 g) was treated with water (10 ml). The pellets of complex were crushed to a finely pulverized suspension. The precipitate was filtered and dried. Crystallization from 10 ml of benzene gave 2 g (69.3% of theory) of the ammonium salt of diphenylborenic acid with m.p. 106-108° (with decomposition). The melting point of the substance was not depressed in admixture with the ammonium salt of diphenylborenic acid [6].

Di-α-naphthylmethylaminoboron. A solution of 4.5 g (0.015 mole) of di-α-naphthylboron chloride in 60 ml of absolute benzene was placed in a four-necked flask equipped with reflux condenser, dropping funnel, and nitrogen admission tube. Into the chloride solution was stirred a solution of 0.9 g (0.03 mole) of methylamine in 10 ml of benzene. Slight heat was generated and methylamine hydrochloride came down (1.1 g, m.p. 226-228°). The precipitate was filtered, and the greater part of the benzene distilled off from the mother liquor. Isopentane was then added. After the mass had been left to stand, 3.6 g of di-α-naphthylmethylaminoboron (81% of theory) crystallized in the form of a colorless, crystalline substance; m.p. (in sealed capillary) 104-106°. Found: C 85.53; 85.36; H 6.16; 6.17; B 3.52; 3.67; N 4.77; 4.57%; M 292.4; 280.7. $C_{21}H_{18}BN$. Calculated: C 85.44; H 6.14; B 3.66; N 4.74%; M 295.17. Di-α-naphthylmethylaminoboron gradually oxidizes in the air. After standing for one-and-a-half months in the open air, the melting point fell to 98-100°. The amine does not react with water at room temperature, but it hydrolyzes when heated; 0.4 g of di-α-naphthylmethylaminoboron was heated with water at 100° for 1 hr to give 0.1 g of naphthalene (m.p. 80°) and 0.2 g of α-naphthylboric acid (m.p. 200-203°).

Di-α-naphthylphenylaminoboron. Under the preceding conditions, 2 g (0.007 mole) of di-α-naphthylboron chloride, dissolved in 40 ml of benzene, and 1.2 g of aniline, dissolved in 10 ml of benzene, gave 1.9 g of di-α-naphthylphenylaminoboron (81.4% of theory) in the form of colorless crystals. M.p. 125-127° (from a mixture of benzene and isopentane). Found: C 87.59; 87.27; H 5.57; 5.79; B 2.98; 3.19; N 4.18; 4.28%; M 353.47; 347.5. $C_{26}H_{20}BN$. Calculated: C 87.40; H 5.64; B 3.02; N 3.91%; M 357.26.

The experiment also gave 0.78 g of aniline hydrochloride with m.p. 197-198° (no depression in a mixed melting test). Di-α-naphthylphenylaminoboron is easily soluble in benzene and poorly in isopentane. It is very unstable when stored and is hydrolyzed with facility by moist air. Treatment of 1 g of the product with water at room temperature gave 0.7 g of di-α-naphthylboric acid with m.p. 111-114° (no depression in a mixed melting test).

Di-α-naphthylisobutylaminoboron. Reaction under the conditions of the preceding experiment of 5.2 g (0.017 mole) of di-α-naphthylboron chloride with 2.6 g of isobutylamine gave 4.7 g (0.034 mole) of di-α-naphthyl-isobutylaminoboron (80.6% of theory) with b.p. 240-245° (1 mm) in the form of a viscous, colorless oil. Found: C 85.18; 85.40; H 7.09; 7.13; B 3.37; 3.45; N 4.09; 4.29%; M 328.9; 331.3. $C_{24}H_{24}BN$. Calculated: C 85.46; H 7.17; B 3.20; N 4.15%; M 337.2.

The experiment also yielded 2.1 g of isobutylamine hydrochloride with m.p. 175-176° (no depression in a mixed point determination). Di-α-naphthylisobutylaminoboron is readily soluble in benzene, ether, and isopentane; it is unstable when stored. The amine does not react with water at room temperature, but on boiling it breaks down completely to naphthalene, α-naphthylboric acid, and isobutylamine.

Di-α-naphthylaminoboron. Ammonia was passed for an hour through a solution of 1 g of di-α-naphthylboron chloride in 25 ml of absolute benzene. A little heat was generated at the start, and later ammonium chloride came down as a fine dispersion. The latter was filtered. The greater part of the benzene was distilled from the mother liquor and isopentane was added. There was obtained 0.8 g of di-α-naphthylaminoboron (87% of theory) with m.p. 113-114° (sealed capillary) in the form of colorless crystals. Found: B 3.55; 3.99; N 4.97; 4.96%; M 282; 283.6. $C_{20}H_{16}BN$. Calculated: B 3.84; N 4.97%; M 281.

Di-α-naphthylaminoboron is gradually oxidized in the air. The melting point did not change after the substance had been left in an open vessel for a week. After a month the substance melted at 88-90°. At room temperature di-α-naphthylaminoboron does not react with water, but at 100° it hydrolyzes. From 0.3 di-α-naphthyl-aminoboron was obtained 0.1 g of naphthalene (m.p. 80°) and 0.1 g of α-naphthylboric acid (m.p. 200-203°).

Di-α-naphthyldiethylaminoboron. Into a solution of 6.15 g (0.02 mole) of di-α-naphthylboron chloride in 90 ml of absolute benzene was stirred 2.93 g (0.04 mole) of diethylamine in solution in 10 ml of benzene. Slight heat was developed and diethylamine hydrochloride came down. The latter was filtered (2.53 g, m.p. 225-226°). The greater part of the benzene was distilled from the mother liquor and isopentane added to the residue. After standing, the liquid deposited 5.36 g of di-α-naphthyldiethylaminoboron (77.6% of theory) in the form of colorless crystals which after crystallization from a mixture of benzene and isopentane melted at 178-179° (sealed capillary). Found: C 85.46; 85.21; H 7.19; 7.30; B 2.81; 3.01; N 4.20; 4.31% M 335.2; 333.3. $C_{24}H_{24}BN$. Calculated: C 85.46; H 7.17; B 3.20; N 4.15%; M 337.2.

Di-α-naphthyldiethylaminoboron is soluble in benzene, sparingly soluble is ether, and insoluble in isopentane. It is stable to oxygen of the air and remains unchanged after prolonged storage (4 months); it remains unchanged after treatment with cold water and also when heated with water at 100° for an hour.

Action of water on di-α-naphthylboric acid. A mixture of 0.6 g of di-α-naphthylboric acid (m.p. 114-115°) and 10 ml of water was refluxed in a small flask on a water bath for an hour. There was obtained 0.2 g of naphthalene (m.p. 80°) and 0.35 g of α-naphthylboric acid. After crystallization from benzene the acid had m.p. 208-209° (no depression in a mixed melting point test).

SUMMARY

1. Reaction of diphenylboron chloride with aniline gives diphenylphenylaminoboron.

2. Primary and secondary amines act on di-α-naphthylaminoboron chloride to give the corresponding N-substituted di-α-naphthylaminoborons.

3. Di-α-naphthylboron chloride reacts with ammonia to form di-α-naphthylaminoboron; diphenylboron chloride forms diammoniate with ammonia.

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BROMINATION OF SOME AROMATIC ORGANOSILICON COMPOUNDS AND THE REACTIVITY OF THE RESULTING BROMIDES

E. A. Chernyshev and N. G. Tolstikova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

It was recently shown [1] that bromination of benzyltrichlorosilane and β-phenylethyltrichlorosilane with bromine in presence of metallic iron leads to their monobromo derivatives with the bromine only in the para-position. Continuing this investigation in our present work, we studied the influence of alteration of the character of the silyl group (with gradual replacement of the chlorine atoms at the silicon by alkyl radicals) on the rate and direction of bromination. A series of compounds $C_6H_5CH_2Si(R)_nCl_{3-n}$ (n = 1-3) was brominated. The position of the bromine atom in the aromatic ring was established with the help of infrared spectra. Bromination of benzylethyldichlorosilane was found to give only the para-isomer and a very small quantity of meta-isomer. Finally, bromination of benzyltrimethylsilane gave the para- and meta-isomers in approximately equal amounts. In the $C_6H_5CH_2Si(C_2H_5)_nCl_{3-n}$ series (n = 0-3) only para-isomers are formed, irrespective of the number of chlorine atoms or alkyl radicals at the silicon. Results are set forth in Table 1.

TABLE 1

Compound brominated	Isomer obtained
$Cl_3SiCH_2C_6H_5$	Para
$C_2H_5SiCl_2CH_2C_6H_5$	"
$(C_2H_5)_2SiClCH_2C_6H_5$	Para > meta
$(CH_3)_3SiCH_2C_6H_5$	Para: meta = 1:1
$Cl_3SiCH_2CH_2C_6H_5$	Para
$C_2H_5SiCl_2CH_2CH_2C_6H_5$	"
$(C_2H_5)_3SiCH_2CH_2C_6H_5$	Para

In a study of the reactivity of aromatic silicohydrocarbons with various positions of the aromatic ring relative to the silicon atom, in the nitration reaction we had observed [2] that trimethylbenzylsilane has an exceptionally high reactivity whereas its two immediate homologs are very much less reactive. Conjugation of the Si-C bond with the aromatic ring when the latter was in the β-position to the silicon atom was held responsible for this phenomenon. The same effect should be manifested in the bromination reaction. Mixtures of equimolar quantities of benzyltrichlorosilane and benzyltrimethylsilane and of benzyltrichlorosilane and β-phenylethyltrimethylsilane were brominated under identical conditions. Unfortunately the bromination of phenyltrimethylsilane could not be investigated due to cleavage of the $Si-C_{phenyl}$ group by bromine. Benzyltrimethylsilane was found to be 28 times and β-phenylethyltrimethylsilane only 2.34 times more active than benzyltrichlorosilane. In our opinion the increased reactivity of benzyltrimethylsilane is associated with conjugation of the Si-C bond with the aromatic ring.

We had shown earlier that a decisive influence on the magnitude of the effect of conjugation of the double bond with the Si-C bond in allylsilane chlorides [3] $CH_2 = CHCH_2SiR_nCl_{3-n}$ (n = 0-3), and also of the C-Cl and Si-C bonds in β-chloroethylsilane chlorides [4] $ClCH_2CH_2SiR_nCl_{3-n}$ (n = 0-3) is exerted by the number of chlorine atoms at the silicon. When three chlorine atoms are present (n = 0) the conjugation effect is at a minimum. We should therefore expect no influence of the effect of conjugation of the Si-C bond with the aromatic ring in benzyltrichlorosilane. This assumption is indirectly confirmed by the fact that benzyltrimethylsilane is brominated 28

times faster than benzyltrichlorosilane. For final confirmation we brominated the following pairs of compounds: phenyltrichlorosilane and benzene, benzyltrichlorosilane and benzene, β-phenylethyltrichlorosilane and benzene. In the case of the first pair, only the benzene was brominated (the phenyltrichlorosilane was recovered unchanged). Benzyltrichlorosilane was brominated 4.7 times and β-phenylethyltrichlorosilane 5.8 times faster than benzene.

Consequently the reactivity in the $Cl_3Si(CH_2)_n$ ⟨☐⟩ series gradually increases with n, i.e. in all cases only the inductive effect of the trichlorosilyl group comes into play, and in benzyltrichlorosilane the effect of conjugation of the Si–C bond with the aromatic ring is completely suppressed.

It was shown earlier that in the chloroalkyltrialkylsilane series $R_3Si(CH_2)_nCl$, α-halides (n = 1) are more reactive with nucleophilic reagents than γ-halides (n = 3) [5]. The reactivity of β-halides (n = 2) could not be studied due to the susceptibility to the so-called β-breakdown.

In the present work we studied the reactivity of aromatic organosilicon halides $R_3Si(CH_2)_n$ ⟨☐⟩ Br

(n = 0 to 2) with nucleophilic reagents. The method of Ufimtsev and Malafeeva was used [6]: A mixture of piperidine and the organosilicon bromide in a sealed ampoule was placed in a thermostat, and the ampoule was rotated at 100° for an hour. After cooling, the content of the ampoule was treated with water, the aqueous layer was separated, the bromide ion brought down with silver nitrate solution, and the quantity of reacted bromide determined gravimetrically. The reactivity of two series of compounds was investigated:

$$(CH_3)_3Si(CH_2)_n \langle \Box \rangle Br \quad \text{and} \quad (C_2H_5)_3Si(CH_2)_n \langle \Box \rangle Br$$
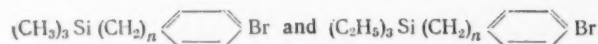
where n = 0-2. Results are set forth in Table 2; in the case of aromatic bromides it was again found that α-bromides (n = 0) are more reactive than γ-bromides (n = 2), although the difference is less marked than in the aliphatic series. Of the compounds investigated, the β-bromides (n = 1) were the least active. This confirms the existence of an effect of the conjugation between the Si–C bond and the aromatic ring in these compounds, for if the inductive effect of the trialkylsilyl group alone had been operative the reactivity of the bromides should have gradually decreased in the sequence α > β > γ.

EXPERIMENTAL

Bromination of benzylethyldichlorosilane. Benzylethyldichlorosilane was prepared by the Grignard reaction from ethyltrichlorosilane (3 moles) and benzylmagnesium chloride (0.5 mole); yield 56%. B.p. 97-100° (5 mm); n_D^{20} 1.5163; d_4^{20} 1.1082.

To 58 g (0.264 mole) of benzylethyldichlorosilane in a three-necked flask, equipped with stirrer and dropping funnel, was added 2-3 g of fine iron turnings, prepared on a lathe. The reaction was performed at room temperature which was maintained by a water bath. In the course of 3 hr dropwise addition of 42 g (13.5 ml)(0.264 mole) of bromine was made. After the bromine had been added, dry nitrogen was blown through the reaction mixture for removal of hydrogen bromide and unreacted bromine. After filtration, the mixture was fractionally distilled. p-Bromobenzylethyldichlorosilane was isolated with b.p. 132-135° (4.5 mm); n_D^{20} 1.5491; d_4^{20} 1.4170; yield 53.9 g (68%). The product was ethylated by C_2H_5MgBr, and p-bromobenzyltriethylsilane was obtained in 78% yield; b.p. 138-140° (5 mm); n_D^{20} 1.5324; d_4^{20} 1.1570. According to the literature [1], p-bromobenzyltriethylsilane has b.p. 140.5-141° (5 mm); n_D^{20} 1.5324; d_4^{20} 1.1560. The compound was identified as the para-isomer through the infrared spectrum.

Bromination of benzyldiethylchlorosilane. Diethyldichlorosilane (2 moles) was reacted with benzylmagnesium chloride (0.5 mole) to give benzyldiethylchlorosilane in 63% yield; b.p. 112° (5 mm). Bromination was performed in the same apparatus and under the same conditions as for bromination of benzylethyldichlorosilane. Reaction components were 43 g (0.202 mole) of benzyldiethylchlorosilane and 32.5 g (10 ml) (0.202 mole) of bromine. Fractional distillation gave a fraction of monobromo derivatives of benzyldiethylchlorosilane with b.p. 145-153° (5 mm); n_D^{20} 1.5429; d_4^{20} 1.2984 in the amount of 35.4 g; yield 61%.

The bromide was ethylated with C_2H_5MgBr and bromobenzyldiethylsilane was obtained in 70% yield; b.p. 135-140° (5 mm); n_D^{20} 1.5321; d_4^{20} 1.1582. The infrared spectrum of the product showed it to be mainly para-isomer with about 15% of meta-isomers.

Bromination of benzyltrimethylsilane. Benzyltrimethylsilane was prepared by the Grignard reaction from trimethylchlorosilane and benzylmagnesium chloride in 84% yield; b.p. 184-185° (750 mm); n_D^{20} 1.4942; d_4^{20} 0.8660. Bromination of benzyltrimethylsilane was performed in the apparatus and under the conditions employed for bromination of benzylethyldichlorosilane. Amounts taken were 60 g (0.366 mole) of benzyltrimethyl silane and 58.5 g (0.366 mole) of bromine. Fractional distillation gave 60.3 g of monobromo derivative with b.p. 90-91° (4.5 mm); n_D^{21} 1.5299; d_4^{20} 1.1901; yield 67%. Judging by the infrared spectrum of the product, it was a mixture of approximately equal parts of para- and meta-isomers.

Bromination of β-phenylethylethyldichlorosilane. β-Phenylethylethyldichlorosilane was prepared by addition of ethyldichlorosilane to styrene in presence of chloroplatinic acid and had b.p. 106° (4 mm); n_D^{20} 1.5095; d_4^{20} 1.1149. Bromination of β-phenylethylethyldichlorosilane was performed in the apparatus and under the conditions for bromination of benzylethyldichlorosilane. Reactants were 120 g 0.51 mole) of β-phenylethylethyldichlorosilane and 82.4 g (0.51 mole) of bromine. Fractional distillation gave 98.3 g of p-bromo-(β-phenylethyl) ethyldichlorosilane with b.p. 135° (4.5 mm); n_D^{20} 1.5469; d_4^{20} 1.4351; yield 62%. The bromide was ethylated with C_2H_5MgBr to give p-bromo-(β-phenylethyl)-triethylsilane with (73% yield) b. p. 131° (3 mm)- n_D^{20} 1.5228; d_4^{20} 1.1439. According to the literature [1], p-bromo-(β-phenylethyl)triethylsilane has b.p. 149° (4.5 mm); n_D^{20} 1.5248; d_4^{20} 1.1420. Judging by the infrared spectrum, the product is the para-isomer.

Bromination of β-phenylethyltriethylsilane. β-Phenylethyltriethylsilane was obtained by ethylation of β-phenylethyltrichlorosilane with C_2H_5MgBr. It had b.p. 264-265° (750 mm); n_D^{20} 1.4964; d_4^{20} 0.8863. Bromination of β-phenylethyltriethylsilane was carried out in the apparatus and under the conditions used in the experiment with benzylethyldichlorosilane. In the reaction were taken 53 g (0.24 mole) of β-phenylethyltriethylsilane and 38.5 g (0.24 mole) of bromine. Fractional distillation gave 20.3 g of p-bromo-(β-phenylethyl)triethylsilane with b.p. 131° (3.5 mm); n_D^{20} 1.5226; d_4^{20} 1.1463. According to the literature [1] p-bromo-(β-phenylethyl)triethylsilane has b.p. 149° (4.5 mm); n_D^{20} 1.5248; d_4^{20} 1.1420. The infrared spectrum of the product was taken and corresponded to the para-isomer.

Bromination of an equimolar mixture of benzyltrichlorosilane and benzyltrimethylsilane. Bromination was performed in the apparatus and under the conditions employed in the experiment with benzylethyldichlorosilane. Starting components were 45 g (0.2 mole) of benzyltrichlorosilane, 33 g (0.2 mole) of benzyltrimethylsilane, and 16 g (0.2 mole) of bromine. The resulting mixture was fractionated in a 20-plate column to give three fractions: 1st, b. p. 65-75° (4 mm), 55.4 g; 2nd, b.p. 75-85° (4 mm), 12.4 g; 3rd, b.p. 85-130°(4 mm), 13.01 g; residue 1.5 g.

The 1st fraction was a mixture of benzyltrichlorosilane and benzyltrimethylsilane, the 3rd a mixture of bromobenzyltrichlorosilane and bromobenzyltrimethylsilane. The three fractions were separately hydrolyzed by careful addition to water containing ethyl ether. The organic layer was separated from the water and from the resulting resin. After the ether had been removed, the residue of the 1st fraction was benzyltrimethylsilane; n_D^{20} 1.4938; d_4^{20} 0.8668; weight 19.6 g. The residue of the 3rd fraction was bromobenzyltrimethylsilane; weight 12.3 g. The residue from the 2nd fraction (4.4 g) had n_D^{20} 1.5003, equivalent to 3.2 g of benzyltrimethylsilane and 1.2 g of bromobenzyltrimethylsilane. Consequently, at the instant of completion of the reaction, the reaction mixture contained 22.8 g (0.140 mole) of benzyltrimethylsilane, 44.1 g (0.196 mole) of benzyltrichlorosilane, 13.5 g (0.055 mole) of bromobenzyltrimethylsilane, and 0.71 g (0.0023 mole) of bromobenzyltrichlorosilane.

The ratio of the velocity constants of bromination of benzyltrimethylsilane and bromination of benzyltrichlorosilane was calculated from Ingold's formula [7]

$$K_x/K_y = \lg\frac{x}{x_0} \Big/ \lg\frac{y}{y_0},$$

where K_x and K_y are the velocity constants of reaction of substance X and Y; x and y are the final concentrations, and x_0 and y_0 are the initial concentrations in moles of substances X and Y in the reaction mixture. It was found that the $K_{benzyltrimethylsilane}/K_{benzyltrichlorosilane}$ ratio during bromination was 28:1.

Bromination of an equimolar mixture of β-phenylethyltrimethylsilane and benzyltrichlorosilane. Bromination was performed in the apparatus and under the conditions employed in the experiment with benzylethyldichlorosilane. Reaction components were 35.6 g (0.2 mole) of β-phenylethyltrimethylsilane, 45 g (0.2 mole) of benzyltrichlorosilane, and 16 g (0.2 mole) of bromine. The resulting mixture was fractionated in a 20 plate column and three fractions were obtained: 1st b.p. 75-90° (8 mm), 73.5 g; 2nd, b.p. 90-120° (8 mm), 2.8 g; 3rd, b.p. 120-140° (8 mm), 7.8; residue. 0.8 g.

Fraction I was a mixture of β-phenylethyltrimethylsilane and benzyltrichlorosilane; fraction III was a mixture of p-bromo-(β-phenylethyl)trimethylsilane and p-bromobenzyltrichlorosilane. All of the fractions were worked up as in the experiment with a mixture of benzyltrichlorosilane and benzyltrimethylsilane. Judging by the results obtained, at the instant of completion of the reaction the mixture contained 31.8 g (0.17 mole) of β-phenylethyl-trimethylsilane, 43.0 (0.19 mole) of benzyltrichlorosilane, 5.3 g (0.020 mole) of bromo-β-phenylethyl trimethyl-silane, and 2.7 g (0.0088 mole) of bromobenzyltrichlorosilane. The $K_{\beta\text{-phenylethyltrimethylsilane}}/K_{\text{benzyltrichloro-silane}}$ ratio calculated by Ingold's formula was 2.34:1.

TABLE 2

Compound investigated	% of compound reacted
C_6H_5Br	11,54; 11,82
$(CH_3)_3SiC_6H_4Br$	25,51; 25,12
$(CH_3)_3SiCH_2C_6H_4Br$	15,73; 15,11
$(CH_3)_3SiCH_2CH_2C_6H_4Br$	24,23; 23,85
$(C_2H_5)_3SiC_6H_4Br$	17,00; 17,49
$(C_2H_5)_3SiCH_2C_6H_4Br$	11,70; 11,54
$(C_2H_5)_3SiCH_2CH_2C_6H_4Br$	15,03; 14,85

Bromination of an equimolar mixture of benzene and phenyl-trichlorosilane. Bromination was performed in the apparatus and under the conditions employed for the experiment with benzylethyldichloro-silane. Reaction components were 39 g (0.5 mole) of benzene, 105.7 g (0.5 mole) of phenyltrichlorosilane, and 40 g (0.5 mole) of bromine. Fractional distillation gave 10.3 g of benzene; 54.8 g of bromobenzene with b.p. 156° (748 mm), n_D^{20} 1.5600; 102.3 g of phenyltrichlorosilane with b.p. 195-197° (743 mm), n_D^{20} 1.5220; and 4 g of residue. Bromo-phenyltrichlorosilane was not isolated.

Bromination of an equimolar mixture of benzene and benzyl-trichlorosilane. Bromination was performed in the apparatus and under the conditions employed in the experiment with benzylethyldichloro-silane. Reaction components were 16.4 g (0.21 mole) of benzene, 48 g (0.21 mole) of benzyltrichlorosilane, and 16.8 g (0.21 mole) of bromine. Fractional distillation gave 14.2 g (0.182 mole) of benzene; 3.45 g (0.022 mole) of bromobenzene; 28.3 g (0.126 mole) of benzyltrichlorosilane with b.p. 215° (750 mm), n_D^{20} 1.5198; 25 g (0.082 mole) of bromobenzyltrichlorosilane with b.p. 132° (10 mm), n_D^{20} 1.5610; and 0.8 of residue. The $K_{\text{benzyltrichlorosilane}}/K_{\text{benzene}}$ ratio calculated from Ingold's formula was 4.73 : 1.

Bromination of an equimolar mixture of benzene and β-phenylethyltrichlorosilane. The reaction was performed in the apparatus and under the conditions employed in the experiment with benzylethyldichlorosilane. Reactants were employed in the experiment with benzylethyldichlorosilane. Reactants were 23.4 g (0.3 mole) of benzene, 72 g (0.3 mole) of β-phenylethyltrichlorosilane, and 24 g (0.3 mole) of bromine. Fractional distillation gave 21.8 g (0.279 mole) of benzene, 2.25 g (0.014 mole) of bromobenzene, 53.5 g (0.224 mole) of β-phenylethyltrichloro-silane, and 23.2 g (0.073 mole) of bromo-β-phenylethyl trichlorosilane. The $K_{\beta\text{-phenylethyltrichlorosilane}}/K_{\text{ben-zene}}$ ratio calculated from the Ingold formula was 5.8 : 1.

Determination of reactivity of silicoorganic aromatic bromides in the reaction with piperidine. p-Bromophenyl-trimethylsilane was prepared by Grignard reaction from trimethylchlorosilane and p-bromophenylmagnesium bromide in 54% yield and had b.p. 80° (4.5 mm); n_D^{20} 1.5258; d_4^{20} 1.2120. p-Bromophenyltriethylsilane was obtained in 68% yield from triethylchlorosilane and p-bromophenylmagnesium bromide. It had b.p. 149°(14 mm); n_D^{20} 1.5314; d_4^{20} 1.1693. p-Bromobenzyltrimethylsilane was obtained in 72% yield from p-bromobenzyltrichlorosilane and methyl-magnesium bromide. It had b.p. 96° (5 mm); n_D^{20} 1.5289; d_4^{20} 1.1891. p-Bromo-β-phenylethyl trimethylsilane was obtained in 80% yield from p-bromo-β-phenylethyltrichlorosilane and methylmagnesium bromide. It had b.p. 115° (5 mm); n_D^{20} 1.5205; d_4^{20} 1.1662. p-Bromobenzyltriethylsilane and p-bromo-β-phenylethyltriethylsilane were prepared by the procedure of [1].

A weighed quantity of about 0.1 g of the bromide, 1 ml of piperidine, and 0.1 g of $CuSO_4 \cdot 5H_2O$ were placed in an ampoule and mixed. The ampoule was sealed and fixed to the movable shaft of an electric motor which was placed in a glycerol thermostat at 100°. Efficient stirring was achieved by fixing the ampoule to the middle part. After an hour the ampoule was withdrawn from the thermostat and cooled, and its contents poured into 10 ml of water; the ampoule was rinsed out with nitric acid solution. The organic layer was extracted with ether and separated. The aqueous layer was treated with 10% $AgNO_3$ solution. The precipitated AgBr was filtered and analyzed gravimetrically. Experimental results are set forth in Table 2.

SUMMARY

1. The direction of bromination in the ring of benzylalkylchlorosilanes and β-phenylethylalkylchlorosilanes was studied in dependence on the ratio of alkyl radicals to bromine atoms at the silicon atom.

2. The reactivity of benzyltrimethylsilane in the bromination reaction is higher than that of β-phenylethyltrimethylsilane, while for benzyltrichlorosilane the reactivity is intermediate between that of phenyltrichlorosilane and β-phenylethyltrichlorosilane.

3. The reactivity of the bromides $R_3Si(CH_2)_n$ ⬡ Br to the action of piperidine follows the sequence $\alpha > \gamma > \beta$.

4. The results obtained are consistent with the existence of a conjugation effect between the Si-C bond and the aromatic ring of trialkylbenzylsilanes and with the absence of such an effect in trichlorobenzylsilanes.

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ACYLATION OF SILICOHYDROCARBONS AND SYNTHESIS OF SILICON-CONTAINING α-METHYLSTYRENES

E. A. Chernyshev, É. N. Klyukina, and A. D. Petrov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

We recently synthesized p-trimethyl- and p-triethylsilylstyrenes and α-methylstyrenes [1], and we also studied their polymerization and copolymerization and the properties of the resulting polymers [2]. It was shown that the products based on α-methylstyrene have a number of advantages over the styrene-based polymers; in particular their softening point is higher. In the present investigation we undertook the synthesis of silicon-containing α-methylstyrenes $R_3Si(CH_2)_nC_6H_6C(CH_3)=CH_2$ where n=1, 2. In the preceding communication [1] we put forward the following scheme for synthesis of the α-methylstyrenes:

$$R_3Si(CH_2)_n - \langle \rangle - MgBr + CH_3COCH_3 \rightarrow R_3Si(CH_2)_n - \langle \rangle - \underset{\underset{CH_3}{|}}{COH} - CH_3 \rightarrow$$

$$\xrightarrow{-H_2O} R_3Si(CH_2)_n - \langle \rangle - \underset{\underset{CH_3}{|}}{C} = CH_2$$
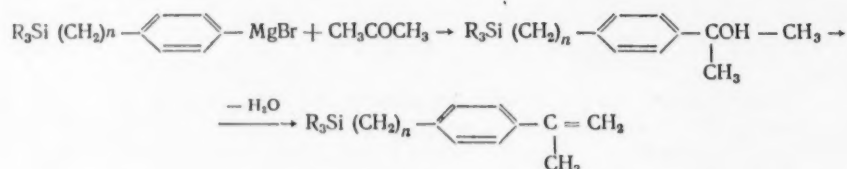
This scheme was satisfactory when n = 0, but when n = 1 or 2 it was found that the organomagnesium compounds were extremely inactive and this caused difficulty in preparation of α-methylstyrenes by this route.

In the present work we made use of another sequence of reactions for preparation of silicon-containing α-methylstyrenes:

$$R_3Si(CH_2)_n - \langle \rangle + CH_3COCl \xrightarrow{AlCl_3} R_3Si(CH_2)_n - \langle \rangle - COCH_3 \xrightarrow{+CH_3MgBr}$$

$$\rightarrow R_3Si(CH_2)_n - \langle \rangle - \underset{\underset{CH_3}{|}}{COH} - CH_3 \xrightarrow{-H_2O} R_3Si(CH_2)_n - \langle \rangle - \underset{\underset{CH_3}{|}}{C} = CH_2$$
$$n = 1, 2.$$
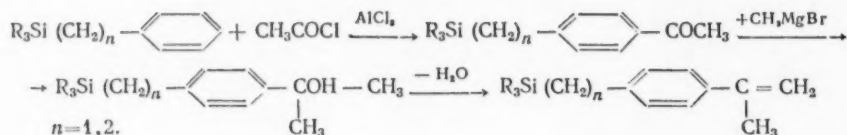
Some years ago, in collaboration with Kulish [3] we developed a method of acylation of trimethylbenzyl-silane by acyl chlorides with the help of $AlCl_3$. In the present work we extended this technique in an improved form to β-phenylethyltrialkylsilanes.

It was recently shown that in the $R_3Si(CH_2)_n - \langle \rangle$ series, compounds with n = 1, i.e. with the aromatic ring in the β-position to the silicon atom, are very much more reactive than their neighboring homologs to the action of electrophilic reagents (for example nitrating [4] and brominating [5] agents). Anomalies have also been observed in the spectra [6] and dipole moments [7] of this family of compounds. In our opinion these effects are due to the occurrence of conjugation between the Si-C bond and the aromatic ring in the β-position to the Si

atom. It was therefore considered of interest to clarify, incidental to the main objective of the present work, the reactivity of benzyl- and β-phenylethyltrialkylsilanes in acylation. Unfortunately the acylation of phenyltrialkylsilanes in presence of $AlCl_3$ is impossible due to cleavage of the $Si-C_{phenyl}$ bond by aluminum chloride.

We made use of the method of competing reactions for determination of the relative reactivities of trimethylbenzylsilane and β-phenylethyltrimethylsilane. An equimolar mixture of benzene and trimethylbenzylsilane (or β-phenylethyltrimethylsilane) was acylated with one mole of caproyl chloride in presence of one mole of aluminum chloride. We chose caproyl chloride because we then have an adequate difference between the boiling points of the products and their separation is facilitated. From the results of the reaction we determined the final concentrations of benzene and silicohydrocarbon. From Ingold's formula [8] $k/k_{benzene} = \log (x/x_0)/\lg (y/y_0)$, ($k$ = velocity constant of the silicohydrocarbon reaction, $k_{benzene}$ = velocity constant of the benzene reaction; x, x_0, y, y_0 are the initial and final concentrations of silicohydrocarbon and benzene), we calculated the reactivity of the silicohydrocarbon (relative to benzene). It was found that in the acylation reaction trimethylbenzylsilane is approximately 24 times more active than benzene, whereas β-phenylethyltrimethylsilane is only approximately 16 times more active than benzene in the same reaction. The greater reactivity of benzylsilane in comparison with its nearest homolog is likewise evidently due to conjugation of the Si-C bond with the aromatic ring.

Silicoorganic ketones were prepared in yields of up to 70% during a study of competing reactions, whereas in the preceding investigation [3] our yields of ketones did not exceed 35%. The results led us to the idea that performance of the reaction in benzene solution should lead to higher yield of silicoorganic ketones. This expectation was fulfilled when the molar ratio of silicohydrocarbon to benzene was between 1:2 and 1:4, the yield of the desired ketone being considerably increased. Some comparative data for yields of ketones by the old and new methods are given in Table 1.

All of the ketones described below were obtained by performing the reaction in benzene solution. Formulas, yields, and properties of the resulting ketones are set forth in Table 2. From the para-substituted acetophenones (i.e. ketones 1,2,3,4 in Table 2) the corresponding alcohols were prepared by Grignard reaction (using CH_3MgCl) and dehydration of the latter to the corresponding styrenes was attempted. Partial dehydration of the alcohols took place even during the reaction and during fractional distillation, and only in two cases out of the four could we isolate alcohols in a sufficiently pure form; their formulas and properties are set forth in Table 3.

TABLE 1

Silicone-containing ketone	% yield in absence of benzene	% yield (reaction in benzene solution)
$(CH_3)_3SiCH_2C_6H_4COCH_3$	28	70
$(CH_3)_3SiCH_2CH_2C_6H_4COCH_3$	17	72
$(C_2H_5)_3SiCH_2C_6H_4COCH_3$	20	35
$(CH_3)_3SiCH_2C_6H_4COC_5H_{11}$	32	76

The alcohols, and also the low-boiling fractions obtained by their fractionation (consisting of mixtures of styrenes and alcohols), were subjected to dehydration. Alcohols in which three of the silicon valences were saturated by methyl radicals were quantitatively dehydrated even during boiling with acid potassium sulfate. On the otherhand, alcohols in which three silicon valences are saturated by ethyl radicals were only partly dehydrated by $KHSO_4$. They were dehydrated by passage over Al_2O_3 in a quartz tube at 340° and under partial vacuum (160-180 mm). Yields and properties of the resulting styrenes are set forth in Table 4.

EXPERIMENTAL

The silicohydrocarbons used in the work were synthesized by Grignard reaction and had the following properties: benzyltrimethylsilane, b.p. 184-185° (750 mm), n_D^{20} 1.4942, d_4^{20} 0.8659; benzyltriethylsilane, b.p. 249-250° (748 mm), n_D^{20} 1.5088, d_4^{20} 0.8975; β-phenylethyltrimethylsilane, b.p. 208-210° (748 mm), n_D^{20} 1.4862, d_4^{20} 0.8632; β-phenylethyltriethylsilane, b.p. 265-266° (748 mm), n_D^{20} 1.4965, d_4^{20} 0.8866. The same procedure was followed for synthesis of each of the ketones; we therefore give details of only one experiment.

Synthesis of p-trimethylsilylmethylacetophenone. A mixture of 242 g (1.5 mole) of benzyltrimethylsilane and 234 g (3 mole) of benzene was put into a three-necked flask fitted with stirrer and seal, thermometer, and reflux condenser. In the course of two hr addition was made(in ten equal portions with vigorous stirring)of 58.5 g (0.75 mole) of acetyl chloride and 97.5 g (0.75 mole) of aluminum chloride (or else a quantity of acyl chloride and $AlCl_3$ in equimolar ratio to the silicohydrocarbon, in which event the yield of ketone is rather lower although its absolute amount is 1.6-1.8 times larger). The reaction flask was cooled with water so that the temperature of the reaction mixture did not rise above 30°. After the addition of acetyl chloride and $AlCl_3$ had been completed,

TABLE 2

Serial no.	Silicoorganic ketone	Yield in %	B.p. in deg C (p in mm mercury)	n_D^{20}	d_4^{20}	M.p. of 2,4-dinitrophenylhydrazone in °C	Calculated (in %)			Found (in %)		
							C	H	Si	C	H	Si
1	$(CH_3)_3SiCH_2C_6H_4COCH_3$	70	140—141 (14)	1,5254	0,9620	207	69,90	8,73	13,59	69,84 / 69,52	8,68 / 8,72	13,56 / 13,82
2	$(CH_3)_3SiCH_2CH_2C_6H_4COCH_3$	72	152,5—154 (11)	1,5270	0,9648	160	70,90	9,09	12,73	70,86 / 70,54	9,06 / 9,09	12,78 / 12,92
3	$(C_2H_5)_3SiCH_2C_6H_4COCH_3$	35	141—143 (4)	1,5260	0,9633	170	72,58	9,68	11,30	72,42 / 72,36	9,68 / 9,63	11,42 / 11,48
4	$(C_2H_5)_3SiCH_2CH_2C_6H_4COCH_3$	29	158—160 (2)	1,5279	0,9860	110	73,28	9,92	10,70	73,22 / 73,18	9,86 / 9,78	10,53 / 10,64
5	$(CH_3)_3SiCH_2C_6H_4COC_5H_{11}$	76	150—152 (4)	1,5093	0,9280	133	73,28	9,92	10,70	73,18 / 73,06	9,84 / 9,80	10,73 / 10,92
6	$(CH_3)_3SiCH_2CH_2C_6H_4COC_5H_{11}$	69	163—165 (4)	1,5130	0,9297	132	73,91	10,14	10,14	73,96 / 73,58	10,14 / 10,10	10,28 / 10,12
7	$(C_2H_5)_3SiCH_2C_6H_4COC_5H_{11}$	70	212—213 (7)	1,5188	0,9397	102	75,00	10,52	9,21	74,96 / 74,82	10,50 / 10,44	9,25 / 9,32

TABLE 4

Silicoorganic α-methyl-styrene	% yield	B.p. in deg C (p in mm Hg)	n_D^{20}	d_4^{20}	Calculated in %			Found in %		
					C	H	Si	C	H	Si
$(CH_3)_3SiCH_2C_6H_4C=CH_2$ CH_3	42	88 (4)	1,5230	0,8914	76,47	9,80	13,73	76,28 / 76,38	9,70 / 9,68	13,68 / 13,91
$(CH_3)_3SiCH_2CH_2C_6H_4C=CH_2$ CH_3	25	99—101 (3,5)	1,5150	0,8920	77,06	10,09	12,85	76,95 / 76,83	10,12 / 10,03	12,68 / 12,78
$(C_2H_5)_3SiCH_2C_6H_4C=CH_2$ CH_3	40	131—132 (3)	1,5230	0,9108	78,05	10,57	11,38	78,10 / 77,94	10,56 / 10,42	11,36 / 11,48
$(C_2H_5)_3SiCH_2CH_2C_6H_4C=CH_2$ CH_3	44	126,5—127,5 (3)	1,5120	0,9083	78,46	10,77	10,77	78,54 / 78,63	10,69 / 10,73	10,84 / 10,92

TABLE 3

Silicoorganic alcohol	B.p. in °C (p in mm Hg column)	n_D^{20}	d_4^{20}	OH in %	
				calcu-lated	found
$(CH_3)_3SiCH_2C_6H_4C(OH)CH_3$ | CH_3	125—127 (4)	1,5120	0,9348	7,65	7,48; 7,56
$(C_2H_5)_3SiCH_2CH_2C_6H_4C(OH)CH_3$ | CH_3	146—150 (3)	1,5265	0,9677	6,11	6,02; 5,94

stirring was continued for another 30-40 min at room temperature, after which the mass decomposed by pouring onto crushed ice. The organic layer was extracted with ether, dried, and fractionated to give 225 g of benzene, 134.3 g of trimethylbenzylsilane with b.p. 185-188° (750 mm), and 105.3 g of p-trimethylsilylmethylacetophenone with b.p. 140-141° (14 mm), n_D^{20} 1.5254, d_4^{20} 0.9620. Yield of ketone 70% of theory; m.p. of 2.4-dinitrophenyl-hydrazone of the ketone 207°. Formulas, yields, properties, and analyses of the synthesized ketones are set forth in Table 2.

Acylation of an equimolar mixture of benzyltrimethylsilane and benzene. The reaction was carried out in the apparatus of the preceding experiment. The flask was charged with 164 g (1 mole) of benzyltrimethylsilane and 78 g (1 mole) of benzene. In the course of 2.5 hr at 20-30° 134.5 (1 mole) of caproyl chloride and 133.3 g (1 mole) of aluminum chloride were added in ten equal portions. The mixture was then stirred at 30° for another 3 hr, after which it was decomposed by pouring onto crushed ice. The organic layer was extracted with ether, dried, and fractionated in a 30-plate column. There were obtained 73.4 g (0.928 mole) of benzene with b.p. 79.5-80°; 26.7 g (0.163 mole) of benzyltrimethylsilane with b.p. 54.5-55° (4 mm); 0.8 g of a fraction with b.r. 55.5-95° (4 mm); 1.3 g (0.0016 mole) of benzyltrimethylsilane with b.p. 95-95.3° (4 mm), n_D^{20} 1.5060 n_D^{20} 1.5060; no depression of melting point of the 2,4-dinitrophenylhydrazone in admixture with the 2,4-dinitrophenylhydrazone of authentic amylphenyl ketone); 1.2 g of a fraction with boiling range of 95.3-152° (4 mm); 192.5 g (0.734 mole) of p-tri-methylsilylmethylphenylamyl ketone with b.p. 152-153.5° (4 mm), n_D^{20} 1.5100, d_4^{20} 0.9292, m.p. of 2,4-dinitro-phenylhydrazone 133°; 37.3 of high-boiling residue.

The high-boiling residue consisted of polyketones. Allowing for the recovery of 73.4 g of benzene, we can reasonably assume that the whole of the residue was formed from benzylmethylsilane through the monoketone stage. Consequently, at the final instant of the reaction the mixture contained 73.4 g or 0.928 mole of benzene and 26.7 g or 0.163 mole of benzyltrimethylsilane. The $k_{benzyltrimethylsilane}/k_{benzene}$ ratio, calculated from Ingold's formula [8] was 24:1.

Acylation of an equimolar mixture of β-phenylethyltrimethylsilane and benzene. The reaction was per-formed in the apparatus and under the conditions of the preceding experiment. Reaction components were 178 g (1 mole) of β-phenylethyltrimethylsilane, 78 g (1 mole) of benzene, 134.5 g (1 mole) of caproyl chloride, and 133.3 g (1 mole) of aluminum chloride. Fractionation in a 30-plate column gave 71.8 g (0.908 mole) of benzene with b.p. 79-80°; 38.4g (0.216 mole) of β-phenylethyltrimethylsilane with b.p. 69-70° (4 mm), n_D^{20} 1.4872; 1.8 g of a fraction with a boiling range of 70.5-94.5° (4 mm); 2.8 g (0.036 mole) of amylphenyl ketone with b.p. 94.5-95.5°, n_D^{20} 1.5068, m.p. of 2,4-dinitrophenylhydrazone 153° (no depression in admixture with an authentic speci-men of amylphenyl ketone); 2.1 g of a fraction with a boiling range of 95.5-163° (4 mm); 189.8 g (0.69 mole) of p-trimethylsilylethylphenylamyl ketone with b.p. 163-164.5° (4 mm), n_D^{20} 1.5138, d_4^{20} 0.9285, m.p. of the 2,4-di-nitrophenylhydrazone 132°; 40.8 g of high-boiling residue.

The high-boiling residue was a polyketone, evidently formed mainly from the silicohydrocarbon via the monoketone. Consequently at the final instant of reaction the reaction mixture contained 71.8 g or 0.908 mole of benzene and 38.4 g or 0.216 mole of β-phenylethyltrimethylsilane. The $k_{β-phenylethyltrimethylsilane}/k_{benzene}$ ratio calculated from Ingold's formula [8] was 16:1.

Preparation of p-(trimethylsilylmethyl)phenyldimethyl carbinol. All of the alcohols were prepared from the ketones by the same procedure. Only one typical experiment will therefore be described. Reaction was effected in

a three-necked flask fitted with stirrer and seal, reflux condenser, and dropping funnel. Methylmagnesium chloride was prepared in the apparatus from CH_3Cl and 10 g (0.42 mole) of Mg in 200 ml of absolute ether. In the course of an hour at 20-30° 40 g (0.19 mole) of p-(trimethylsilylmethyl)acetophenone was added to the Grignard reagent. The mixture was thereupon stirred for an hour at room temperature and for 30 min at the boiling point of ether. It was then decomposed with ice. The ethereal layer was separated, dried with Na_2SO_4, and distilled. Partial dehydration occurred during the fractionation. There was obtained 8.8 g of a fraction with a boiling range of 90-125° (4 mm), consisting of a mixture of the corresponding styrene and carbinol and 16.1 g of p-(trimethylsilylmethyl)-phenyldimetnyl carbinol. In the same way it was possible to isolate p-(triethylsilylethyl)phenyldimethyl carbinol. The properties of these two alcohols are set forth in Table 3. In the two other cases only a mixture of the corresponding styrenes and alcohols was isolated.

Dehydration of p-(trimethylsilylmethyl)phenyldimethyl carbinol. A Favorskii flask equipped with a sloping condenser was charged with 16 g of p-(trimethylsilylmethyl)phenyldimethylcarbinol, 1 g of hydroquinone, and 3.5 g of $KHSO_4$. The heated mixture evolved water which gradually distilled off. After water had ceased to come off, the reaction was stopped, and the mixture dried over Na_2SO_4. Fractional distillation gave 6.2 g of p-(trimethyl-silylmethyl)-α-methylstyrene with b.p. 88-89° (4 mm), n_D^{20} 1.5230, d_4^{20} 0.8914; yield 42%. The mixture obtained in the synthesis of p-(trimethylsilylethyl)phenyldimethyl carbinol was similarly dehydrated. Alcohols with ethyl radicals at the silicon were dehydrated over Al_2O_3 by the procedure described earlier [1]. Experimental results are set forth in Table 4.

SUMMARY

1. Improvements were effected in the earlier method of acylation of aromatic silicohydrocarbons which enabled preparation of the corresponding ketones in yields of up to 70%.

2. Benzyltrimethylsilane is acylated 24 times faster and β-phenylethyltrimethylsilane only 16 times faster than benzene. This effect is associated with conjugation of the Si-C bond with the aromatic ring in benzyltrimethyl-silane.

3. Some para-substituted silicon containing α-methylstyrenes have been synthesized.

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TRIS(TRIORGANOSILYL)BORATES

N. F. Orlov, B. N. Dolgov, and M. G. Voronkov

Institute of Silicate Chemistry, Academy of Sciences USSR

Silicoorganic derivatives of boron containing the Si-O-B bond have attracted the attention of a number of investigators in very recent times [1-20]. This interest is due above all to the possibility of utilization of boro-silicoorganic compounds, for example as water-resistant [1], electrically insulating [2], and heat-resistant [3-4] coatings. Boric oxide [5], trialkyl borates [6, 7] and boric acid [8] are widely known as catalysts for polymerization of polysiloxanes based on the intermediate formation of compounds containing Si-O-B bonds. The use of boron compounds in syntheses of arylhalosilanes is also probably associated with the formation of silicoorganic derivatives of boron [9], and this theory is supported by the ability of tris(trimethylsilyl) borate to catalyze the arylation of hydrochlorosilanes [10, 11].

During the development of methods of synthesis of various silicoheteroorganic compounds (see for example [12, 13]) it seemed of interest to us to supplement the previously developed methods of preparation of triorgano-silylesters of boric acid-tris(triorganosilyl) borates-[14-16]-by new methods. Krieble's patented claim [14, 15] of the possibility of synthesis of tris(trimethylsilyl) borate by reaction of boric acid with trimethylethoxysilane was not subsequently confirmed although a similar method had been used successfully [16] for preparation of higher tris(trialkylsilyl) borates. One of us has described [16] methods of preparation of tris(trialkylsilyl) borates by reaction of hexaalkyldisiloxanes with boron trioxide, by reaction of trialkylchlorosilanes with boric acid or with tri-alkyl borates, or by transesterification of trialkyl borates with trialkylsilanols. These methods give rather poor yields (20-30%). We developed new methods of synthesis of tris (triorganosilyl) borates that were notable for the excellent yields of 80-95% [12, 17]. The first two of these were based on reactions of triorganosilanols with boron trioxide or boric acid

$$3R_3SiOH + B(OH)_3 \longrightarrow (R_3SiO)_3 B + 3H_2O \tag{1}$$

$$6R_3SiOH + B_2O_3 \longrightarrow 2(R_3SiO)_3 B + 3H_2O \tag{2}$$
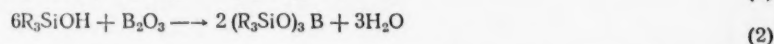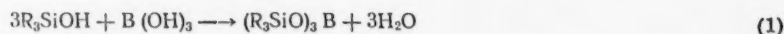
A third method of synthesis of tris(triorganosilyl) borates was based on reaction of triorganosilanes with boric acid in presence of colloidal nickel [12]

$$3R_3SiH + B(OH)_3 \longrightarrow (R_3SiO)_3 B + 3H_2 \tag{3}$$
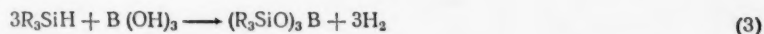
Reactions (1) and (2) were realized by continuous azeotropic distillation of water from the mixture or tri-organosilanols with boric acid or boron trioxide containing an inert solvent (benzene).* It is interesting that under these conditions there was no sign of the competing reaction of condensation of triorganosilanols to hexaorganodi-siloxanes

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* After the main results of the present work had been published [12], references appeared in the literature to the possibility of effecting reactions (1) [18], (2) [19], and (3) [20]. Contrary to our procedure, the water of reaction in the synthesis of tris(triethylsilyl) borate by reaction (2) was removed by binding with anhydrous $CuSO_4$. More-over the yield of $[(C_2H_5)_3SiO]_3B$ was only 40%.

Compound	B.p. deg C (p mm mercury)	d_4^{20}	n_D^{20}	Yield %	Si, % calculated	Si, % found	B, % calculated	B, % found	Prepared by reaction
[(CH₃)₂C₂H₅SiO]₃B*	93—94 (6)	0,8598	1,40.2	47	26,29	—	3,38	3,27; 3,26	1
[(C₂H₅)₂CH₃SiO]₃B	138—140 (6)	0,8773	1,4240	61	23,24	22,87; 22,78	2,98	2,99; 2,86	2
[(C₂H₅)₃SiO]₃B	172—175 (6)	0,8904	1,4378	84	20,83	20,56; 20,49	2,67	2,63; 2,58	1
	165—167 (5)	0,8906	1,4377	92	20,83	20,64; 20,72	2,67	2,72; 2,69	2
	154—155 (4)	0,8915	1,4373	61	20,83	20,77; 20,68	2,67	2,65; 2,62	3
[(C₂H₅)₂C₆H₅SiO]₃B*	250—255 (6)	1,0125	1,5200	85	15,66	14,91; 15,03	2,01	1,98; 2,97	1
[(C₆H₅)₂CH₃SiO]₃B*	320—325 (3)	1,120	1,5850	77	12,95	12,46; 12,34	1,66	—	1
[(C₆H₅)₃SiO]₃B*	Т. пл. 150—	—	—	98,5	10,0я	9,97; 9,89	1,29	—	1

* New compound

which might have been expected to take place. Tris(triorganosilyl) borates were obtained in accordance with reaction (3) by heating of a mixture of triorganosilane and boric acid in presence of colloidal nickel, formed by reaction of nickel chloride, with triorganosilane.

By the three methods mentioned, we prepared six tris(triorganosilyl) borates (see table), four of which were previously unknown.

EXPERIMENTAL

Triorganosilanols were prepared by the method described earlier [21]; their constants agree closely with the literature data; boric acid and boron trioxide ("pure for analysis") were used without further purification. Triethylsilane was synthesized by reaction of ethyldichlorosilane with ethylmagnesium bromide. It had b.p. 108°(757 mm), n_D^{20} 1.4113; d^{20}_4 0.7311.

The silicon in tris(triorganosilyl) borates was determined by mineralization with a mixture of oleum and nitric acid. The precipitated silicic acid was filtered and calcined at 900°. The boron content was found by titration of a weighed sample in aqueous dioxane with 0.1 N NaOH solution in presence of mannitol (phenolphthalein as indicator).

In illustration of the three new methods of synthesis we shall describe the preparation of tris(triethylsilyl) borate by schemes (1), (2), and (3). All of the remaining tris(triorganosilyl) borates were synthesized by the same methods. The physical constants of the substances after further purification, their yields, and analyses are set forth in the table.

Synthesis of [(C₂H₅)₃SiO]₃B by reaction (1). A mixture of 3.1 g of H_3BO_3 (0.06 mole), 19.8 g (0.15 mole) of triethylsilanol and 70 ml of benzene was refluxed for an hour (the condenser was attached to a water collecting trap). After this operation, 2.4 ml of water had separated. The solvent was distilled from the reaction mixture and the residue fractionated in vacuo. There was obtained 17.0 g (84.0%) of tris(triethylsilyl) borate with b.p. 172-174° (6 mm), n_D^{20} 1.4378.

Synthesis of [(C₂H₅)₃SiO]₃B by reaction (2). A mixture of 3.5 g of B_2O_3 (0.05 mole), 39.6 g (0.3 mole) of triethylsilanol, and 80 ml of benzene was heated for 2 hr as indicated in the preceding experiment. After separation of 2.65 ml of water, the benzene was distilled, and the residue distilled in vacuo to give 37.0 g (92.0%) of tris(triethylsilyl) borate with b.p. 165-167° (5 mm), n_D^{20} 1.4377.

Synthesis of [(C₂H₅)₃SiO]₃B by reaction (3). A mixture of 4.32 g (0.07 mole) of H_3BO_3, 2.8 g (0.24 mole) of triethylsilane, and 0.01 g of colloidal nickel was refluxed for 14 hr. After this period the temperature of the reaction mixture had risen to 148° and 4.5 liters of hydrogen had been released. Fractional distillation in vacuo gave 17.0 g (61.0%) of tris(triethylsilyl) borate with b.p. 154-155° (4 mm); n_D^{20} 1.4373.

SUMMARY

Three new methods were developed for synthesis of tris(triorganosilyl) borates, based on reaction of triorganosilanols with boron trioxide or with boric acid, and on reaction of H_3BO_3 with triorganosilanes. These methods were employed for preparation of six compounds of this type, of which four were previously unknown.

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ADDITION OF ALKYLCHLOROSILANES TO UNSATURATED COMPOUNDS
IN PRESENCE OF CHLOROPLATINIC ACID

V. A. Ponomarenko, V. G. Cherkaev, and N. A. Zadorozhnyi

In preceding communications [1-6] we had already encountered some characteristic features of the addition of silanes to unsaturated compounds in presence of platinized carbon. These features were concerned with the influence on the yields of the inductive and (in part) steric effects of silyl groups during additions, the screening of the double bond of the unsaturated compound, of the reaction mechanism, of the reaction conditions, and other factors. The objective of the present work was to clarify to some extent the influence of the same factors in addition reactions in presence of another catalyst-chloroplatinic acid.

We made use of our earlier method [4,5] of competing addition of silanes to ethylene for the purpose of establishing the influence of the nature and number of groups and atoms attached to the Si atom on the relative activity of silanes. All experiments were performed under identical conditions (see Table 1 and Experimental). Results of these experiments are set forth in Table 1. These data at once show that the investigated silanes can be arranged in the following sequence in respect of their activity with ethylene in presence of chloroplatinic acid:

$$(CH_3)(Cl)_2SiH > (CH_3)(C_2H_5)(Cl)SiH > (C_2H_5)(Cl)_2SiH >$$
$$> (C_3H_7)(Cl)_2SiH > (CH_3)(C_2H_5)_2SiH > Cl_3SiH > (C_2H_5)_3SiH.$$
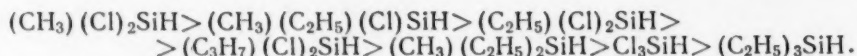
The following facts emerge when we compare the above sequence with the activity sequence $(CH_3)(C_2H_5) \cdot SiH > (CH_3)(C_2H_5)(Cl)SiH > (C_2H_5)(Cl_2)SiH > Cl_2SiH_2$ that we found in the addition to the ethers $CH_2=CHCH_2OCF_2CF_2H$ and $CH_2=CHCH_2OCF_2CF(Cl)H$ in presence of platinized carbon at 160°: 1) addition of alkylchlorosilanes to ethylene in presence of H_2PtCl_6 at 20-40° depends not only on the inductive influence of the chlorine atoms and alkyl groups attached to Si, but also in great measure on the spatial characteristics of these atoms and groups; 2) in presence of platinized carbon, which involves reaction under more drastic conditions, the steric factor plays a less important part; 3) the reaction of competing addition of silanes to ethylene in presence of H_2PtCl_6 differs from the competing addition of the same silanes to $CH_2=CHCH_2OCF_2CF_2H$ and $CH_2=CHCH_2CF_2CF(Cl)H$ in presence of platinized carbon to the extent that there are no appreciable signs of "activation" of addition of silanes of the R_3SiH type in presence of alkylchlorosilanes of the type of $RSiHCl_2$, R_2SiHCl or Cl_3SiH.

No direct relation can be found if we attempt to compare the above activity sequence with data for the electronegativity of the X_3Si groups (X = R, Cl) (see Table 2) which can be determined from the vibration frequencies of the Si-H bond in these compounds [7]. This can only be explained on the assumption that in our case that the activity of alkylchlorosilanes is influenced simultaneously by two factors: the electronegativity and the size of the atoms and groups attached to the silicon. An increase in the size and number of organic radicals lower the activity of alkylchlorosilanes in the addition reaction.

Examples of a similar type are known in organic chemistry. The results of a study of the kinetics of nucleophilic substitution of iodides and bromides of the type of X_3-CH_2-Y (where X = H, F, CH_3 and Y = I or Br) [8] show,

TABLE 1

Results of Competing Addition of Silanes to Ethylene[*]

Silane	Cl, Cl—SiH, CH₃	Cl, CH₃—SiH, C₂H₅	Cl, Cl—SiH, C₂H₅	Cl, Cl—SiH, C₃H₇	CH₃, C₂H₅—SiH, C₂H₅	Cl, Cl—SiH, Cl	C₂H₅, C₂H₅—SiH, C₂H₅	Position in activity series
Cl, Cl—SiH, CH₃		77 : 37	54 : 35	—	111 : 17	—	—	1
Cl, CH₃—SiH, C₂H₅	37 : 77		83 : 71	107 : 29	←	—	—	2
Cl, Cl—SiH, C₂H₅	35 : 54	71 : 83		40 : 32	«3»>«5»	98 : 30	105 : 16	3
Cl, Cl—SiH, C₃H₇	—	29 : 107	32 : 40		—	—	—	4**
CH₃, C₂H₅—SiH, C₂H₅	17 : 111	—	«5»<«3»	—		121 : 23	53 : 8	5
Cl, Cl—SiH, Cl	—	—	30 : 98	—	23 : 121		117 : 5	6
C₂H₅, C₂H₅—SiH, C₂H₅	—	—	16 : 105	—	8 : 53	5 : 117		7

[*] The figures in Table 1 show the yield of addition products in millimoles. In each case the ratio of silanes, the ethylene pressure, and the quantity of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were identical (see Experimental).

** The place of $C_3H_7SiHCl_2$ in the activity series of the silanes was established only in relation to the first three members of the series.

for example, that just as in our case the accumulation of electronegative fluorine atoms and of considerably less electronegative methyl groups in the β-position to the C-I or C-Br bond leads to an identical result—a sharp drop in the rate of substitution. In the one case this reduction is due to the strong inductive effect of the fluorine atoms, in the other it is due mainly to the steric effect of the alkyl groups.

In presence of platinized carbon the rate and direction of the addition reaction is also governed to a considerable extent, as we have already reported [3,9,10], by the structure of the unsaturated compound. It may be noted in connection with the character of the radicals at the double bond of the unsaturated compounds (their electronegativity and steric effect) that screening of the double bond by radicals or atoms with a large steric effect leads to a lower rate of addition of silanes and to a decrease in the yield of reaction products. Replacement of platinized carbon by chloroplatinic acid certainly leads to considerably better results, but the characteristic influence of the structure of the unsaturated compound noted above is retained. The data of Tables 3 to 6 thus enables us to arrange ethylene and its fluorine-substituted derivatives in the following sequence of their ability to combine with silanes in presence of H_2PtCl_6 or platinized carbon:

$$CH_2{=}CH_2 > CH_2{=}CF_2 > CF_2{=}CF(Cl) > CF_2{=}CF_2.$$
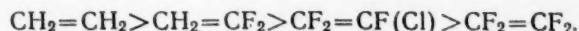
Of very great importance for an understanding of the laws of addition is the elucidation of the mechanism of interaction of the Si-H bond with the multiple bond of an unsaturated compound in presence of H_2PtCl_6 and Pt on supports.

TABLE 2

Electronegativity of X_3Si Groups in X_3SiH

X_3Si- group	Vibration frequency of Si-H bond in cm^{-1}	Electronegativity [7]
Cl_3Si-	2257	2,24
$(CH_3)(Cl)_2Si-$	2214*	2,19
$(C_2H_5)(Cl)_2Si-$	2204	2,18
$(C_3H_7)(Cl)_2Si-$	2206	2,19
$(CH_3)(C_2H_5)(Cl)Si-$	2161*	2,13
$(C_2H_5)_2(CH_3)Si-$	2103*	2,07
$(C_2H_5)_3Si-$	2098	2,07
$(C_2H_5)(C_3H_7)_2Si-$	2100*	2,07

* The spectra of these compounds were taken by N. S. Andreeva.

Some investigators [11-13] have drawn attention to the paucity of the data at the present time available for a conclusive solution of this problem. However, on the basis of certain indirect evidence (inter alia the sequence and stereospecificity of addition, non-suppression of the reaction by inhibitors of radical processes) they assume an ionic mechanism of addition. This theory was argued with particular force by Benkeser and Hickner in one of their recent papers[13].

Our last results on competing addition of silanes to polyfluoroethylallyl ethers in presence of platinized carbon do not so definitely refute the possibility of a radical mechanism [5]. They point on the contrary to the occurrence of just this specific radical mechanism. In our opinion this specificity consists in the localization at the surface of the catalyst a process that implies the following consequences: 1) Influence (evidently different for different substances) of radical reactions on the absorptivity of reactants, or end products, and also of the inhibitors sometimes introduced; the rates of formation and the activities of radicals on such a surface will

TABLE 3
Addition of CH_3SiHCl_2 to $CF_2=CH_2$

Expt. no.	Taken into reaction			Quantity of catalyst in g	Conditions of experiment			Products isolated in g						Yield of $CH_3Si(Cl)_2$ $C_2H_3F_2$ in %
	CH_3SiHCl_2 in g	$CH_2=CF_2$ in g	catalyst		temp. in °C	max. pressure in atm.	high boiling products	$C_2H_2F_2$>$SiCl_2$ / CH_3	C_2H_5>$SiCl_2$ / CH_3	CH_3SiFCl_2	CH_3SiCl_3	CH_3SiHCl_2	High-boiling point	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	124	43	H_2PtCl_6	0,25*	160	34	1,6	61	—	12	3	24	18	39
2	115	65	H_2PtCl_6	0,25*	160	40	**	32,5	6,4	35	5	0	18,3	18
3	115	41	0,05% Pt—SiO$_2$	1	160	40	11,5	0	0	0	0	75	—	0
4	116	26	0,5% Pt/C	0,2	160	38	8	13	2	0	1	77	—	21
5	115	51	10% Pt/SiO$_2$	0,2	160	42	11,5	19,5	0	12	0	44	7	18

* Number of milliliters of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol.
** Temperature raised to 160° in the course of 6 hr; during this operation the pressure increased until the temperature rose to 140° and then started to decrease.

TABLE 4

Addition of CH_3SiHCl_2 to $CF_2=CFCl$

Expt. no.	Taken into reaction			Conditions of experiment				Reaction products					Yield of $CH_3Si(Cl)_2CF_2CF_2H$ in %
	CH_3SiHCl_2 in g	$CF_2=CF(Cl)$ in g	Catalyst	weight of catalyst in g	temp. in °C	max. pressure in atm.	reaction duration in hr.	C_4F_2ClH>$SiCl_2$ / CH_2 in g	CH_3SiHCl_2 in g	secondary products			
										CF_2-CFCl / CF_2-CFCl in ml	CH_3SiCl_3 in ml	high-boiling prod. in g	
1	120	92	H_2PtCl_6	1**	160	—	6	55,4	0	0	35	41	23
2	57,5	60	10% Pt/SiO$_2$	0,15	160	50	12,5	8,0	31	5	1	3	15
3	57,5	70	10% Pt/SiO$_2$	1,0	160	52	10,5	5,6	11	5	9	21	6

* Calculated on the reacted CH_3SiHCl_2
** Number of milliliters of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol.

TABLE 5

Addition of CH_3SiHCl_2 to $CF_2=CF_2$

Expt. no.	Taken into reaction				Expt. conditions			Reaction products			
	CH_3SiHCl_2 in g	$CF_2=CF_2$ in g*	Catalyst	amount of catalyst in g	temp. in °C	max. pressure in atm	reaction period in hr.	$CH_3-SiCl_2-CF_2HCF$* in g	CH_3SiHCl_2 in g	high-boiling residue in g	Yield of $CH_3Si(Cl)_2CF_2$ in %**
1	115	49	H_2PtCl_6	0,25***	160	26	12,5	12,5	79	9,3	19
2	82	26	0,05% Pt/SiO$_2$	1,0	160	28	13	12,5****	40	5	16
3	120	33	0,05% Pt/SiO$_2$	0,5	160	25	14	4,5	78	4,5	5,7
4	120	33	10% Pt SiO$_2$	0,15	160	25	74	7,9	60	5,2	7,1
5	117	36	0,5% PdCl$_2$/SiO$_2$	0,2	160	30	11,5	3,6	72	2	5,5

* $CF_2=CF_2$, which contained a polymerization inhibitor, was injected into the autoclave in the form of gas or was introduced in the solid state; in each case it was difficult to proportion the fluoroolefin accurately.

** Calculated on the CH_3SiHCl_2 reacted.

*** Number of milliliters of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ solution in isopropyl alcohol.

**** There was also isolated 6 g of the telomer $CH_3Si(Cl)_2CF_2CF_2CF_2CF_2H$ with b.p. 137,5-138,5° (747.2 mm).

also vary [5]. 2) Since reaction proceeds at the surface, the polymerization of such unsaturated compounds as butadiene, styrene, and acrylonitrile in presence of peroxides, which usually polymerize with facility when silanes are added to them in presence of peroxides, is suppressed to a considerable extent [3, 12]. 3) Surface-oriented cis-addition is observed in place of the trans-addition typical of a homogeneous process[13]. 4) An analogy is observed (although not in all cases) between the sequence of addition in presence of peroxides and the sequence in presence of Pt on supports, the silyl group usually attaching itself to the terminal carbon atom of an unsaturated compound of the type of $CH_2=CH-X$ (X is R, C_6H_5, OR, OCOR, CF_3, CN, etc.). 5) The reaction in some cases culminates in an explosion (the radical process probably passes over into a branched chain reaction that involves the whole mass of reactants) [14].

The possibility of such radical or radical—chain processes in heterogeneous catalysis is now proven [15-17]. This approach moreover permits a better insight into a series of otherwise difficultly understandable heterogeneously catalytic reactions (hydrogenation, deuteration, etc.) [15].

The mechanism of the action of H_2PtCl_6 is undoubtedly more complex than that of supported platinum if only because H_2PtCl_6 is more or less reduced in the course of the reaction.* However a radical mechanism can again be postulated for various reasons: In the case of either H_2PtCl_6 or supported Pt the sequence of addition is the same; in each case we find products of telomerization with $CH_2=CF_2$, $CF_2=CF_2$, and $CF_2=CF(Cl)$; fixation of free radicals takes place on interaction of R_3SiH with H_2PtCl_6 with the help of diphenylpicrylhydrazyl; moreover, platinum is formed during the reaction in presence of H_2PtCl_6. Just as with Pt on supports, a radical mechanism affords a better explanation of the observed facts than an ionic mechanism when H_2PtCl_6 is used. Addition at a heterogeneous catalyst might be represented by the following scheme:

$$H-Si\equiv \;+\; H_2C=CH-X \;\longrightarrow\; H\;\; Si\equiv \;+\; CH_2=CH-X$$

* At room temperature introduction of H_2PtCl_6 solution into a silane leads to reduction only in the case of trialkylsilanes (R_3SiH). Silanes of the type of R_2SiHCl, $RSiHCl_2$, and Cl_3SiH do not reduce H_2PtCl_6 to Pt under these conditions but probably form some sort of complex which is soluble in silanes. Reduction of H_2PtCl_6 by R_3SiH is accompanied by a sudden change of color of diphenylpicrylhydrazyl, evidently due to "fixation" of the resulting radicals ($H\cdot$, R_3Si, etc.):

$$\dot{R} + (C_6H_5)_2N\dot{N}C_6H_2(NO_2)_3 \xrightarrow{H_2PtCl_6} (C_6H_5)_2N\overset{R}{\underset{|}{N}}C_6H_2(NO_2)_3,$$
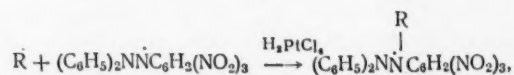
where $R\cdot$ is $H\cdot$, $R_3\dot{Si}$, or other radical.

TABLE 6
Results of Addition of Silanes to Olefins and Acetylene in Presence of H_2PtCl_6

Expt. no.	Silane and solvent	Quantity in g	Unsaturated compound	Quantity of catalyst in ml	Pressure in atm	Reaction temp. in °C	Reaction duration in hrs.	Products isolated	Quantity in g	Yield in %
1	CH_3SiHCl_2	115	$CH_2=CH_2$	0,25	15—2	20—35*	0,5	$CH_3Si(Cl)_2C_2H_5$	117	83
2	CH_3SiHCl_2	58	$CH_2=CHCH_3$	0,3	—	20—30*	1	$CH_3Si(Cl)_2C_3H_7$	64,5	81,5
3	CH_3SiHCl_2	64	$CH\equiv CH$	1,2**	19—8	20—25*	21	$CH_3Si(Cl)_2CH=CH_2$	63	81
4	$C_2H_5SiHCl_2$	45	$CH\equiv CH$	1,5	20	20	7	$C_2H_5SiHCl_2$	32,5	3
	$CHCl_3$	100						$C_2H_5Si(Cl)_2CH=CH_2$		60
								$[(C_2H_5)(Cl)_2SiCH_2]_2$	8	
								$(CH_3)(C_2H_5)Si(Cl)(CH=CH_2)$	5	
5	$CH_3(C_2H_5)SiHCl$	71	$CH\equiv CH$	1,6	10	20—45*	0,08	$[(CH_3)(C_2H_5)(Cl)SiCH_2]_2$	66	83

* Temperature rise due to spontaneous heating during shaking of autoclave.
** Addition did not occur in a similar experiment with 0,06 ml of catalyst (duration of experiment 48 hr).

$$\equiv SiCH_2\dot{C}HX + H-Si\equiv \longrightarrow \equiv SiCH_2CH_2X + Si\equiv$$

where X=alkyl, aryl, OR, CN, CF_3, SiR_3, $SiCl_3$, CH_2SiR_3, etc.

The same process takes place in the case of H_2PtCl_6 if the latter is reduced during the reaction to Pt in the suspended state or deposited on the autoclave walls. If reduction is not complete, then the radical process is probably directed by interactions of the double and Si-H bonds with the inner shells of the complexes $H_2[PtCl_6]$ and $H_2[PtCl_4]$ [18] which can lead to the same result just as in the case of hydrogen tion or hydrations:

$$[PtCl_2 \cdot C_2H_4]_2 + 4H_2 \xrightarrow{\text{room temperature}} 2Pt + 4HCl + 2C_2H_6 \tag{19}$$

$$K\,[PtCl_3 \cdot C_2H_4] + H_2O \xrightarrow{100°} Pt + 2HCl + CH_3CHO + KCl \tag{19}$$
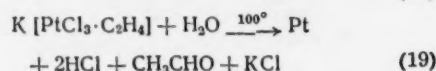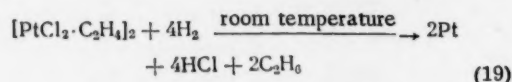
EXPERIMENTAL

Trichlorosilane and methyl- and ethyldichlorosilanes were purified by distillation of the technical products in a 40-plate column; other silanes were prepared from them by the organomagnesium synthesis. Olefins, fluoroolefins, and acetylene were admitted into the autoclave directly from a cylinder without additional purification. Supported palladized and platinized catalysts were prepared in the usual manner from $PtCl_4$ and $PdCl_2$. A solution of chloroplatinic acid was made up from commercial $H_2PtCl_6 \cdot 6H_2O$ and rectified isopropyl alcohol.

The addition reaction was effected in a one-liter, rotating autoclave of EYa-1—T stainless steel. Experiments aiming at determination of relative activities by the method of competing addition were performed in a 0.25-liter autoclave in which the mixture of reactants was shaken. The autoclave was cooled with dry ice before the highly volatile reactants were introduced. Tetrafluoroethylene was admitted in the solid state (cooled with liquid nitrogen) or injected as gas. Trifluorochloroethylene was introduced in the liquefied state. The remaining gases were injected under pressure directly from cylinders. After completion of a reaction, the products were discharged, filtered, and distilled through a 30-40 plate column.

Comparison of activity of silanes by the method of competing addition. A mixture of the two silanes (0.3 mole of each) and 0.15 ml of a 0.001 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol was charged into the autoclave to a pressure of 25-28*. Addition was effected at room temperature (the internal temperature usually rose to 30-40° within a few minutes after admission of ethylene) and was completed after the pressure had

* This corresponds to approximately 0.1 mole of ethylene. The difference between the relative activities becomes less pronounced with large volume of ethylene.

fallen to 0-5 atm. The duration of absorption for different pairs was 0.5 to 24 hr. The reaction products were distilled in an approximately 30-plate column. Experimental results are set forth in Table 1.

Addition of methylchlorosilane to vinylidene fluoride. Conditions and results of the most typical experiments are given in Table 3.

The results show that chloroplatinic acid gives the best results. Satisfactory results were also obtained with 10% Pt/SiO$_2$ and with 0.5% Pt/C. Addition was not observed in presence of 0.01 and 0.05% Pt/SiO$_2$ and PdCl$_2$/SiO$_2$. A high yield of addition product could be obtained with H$_2$PtCl$_6$ when the reactants were heated quickly to the reaction temperature (140-160°); slow heating leads to lower yields due to intensified thermal decomposition of the addition product according to the equation

$$CH_3Si(Cl)_2CH_2CF_2H \rightarrow CH_3SiCl_2F + CH_2{=}CHF,$$
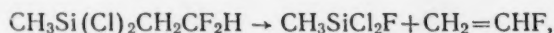
which ultimately gives methylethyldichlorosilane (the most stable product under these conditions). Addition is accompanied by formation of high-boiling products. The fractional distillation curve of these products (Fig. 1) and the empirical analysis of individual fractions show that they are extremely complex mixtures of isomeric telomers. Individual substances could not be isolated
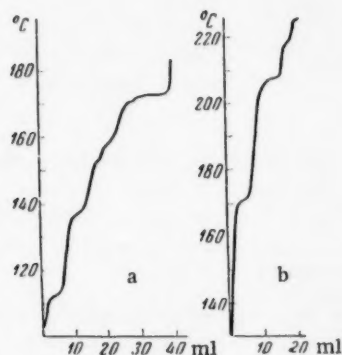
Fig. 1. Curves of fractional distillation at atmospheric pressure of products of telomerization of CH=CF$_2$ with CH$_3$SiHCl$_2$: a) fractionation at 745 mm of 61 g of high-boiling fractions (40-130° at 13-10 mm); b) fractionation at 747 mm of 35 g of high-boiling fractions (130-180° at 10-8 mm).

Addition of methyldichlorosilane to trifluorochloroethylene. Conditions and results of the most typical experiments are set forth in Table 4.

The data show that addition in presence of H$_2$PtCl$_6$ gives a better result than with 10% Pt/SiO$_2$. The fractional distillation curve of the main reaction product (Fig. 2) also shows that it is heterogeneous and evidently consists of a mixture of two isomers. The secondary high-boiling products (fractional distillation curve in Fig. 3) comprises a complex mixture of telomers as reflected in the empirical analyses of individual fractions.

Addition of methyldichlorosilane to tetrafluoroethylene. Conditions and results of the most typical experiments are given in Table 5.

The best yield of product of addition to CF$_2$=CF$_2$ was obtained when using H$_2$PtCl$_6$. However in this case the difference in performance of this catalyst and platinum on supports was less striking than in the two preceding cases, possibly due to the presence in the CF$_2$=CF$_2$ of a polymerization inhibitor which poisoned the catalysts to some extent. Results of fractionation of the products of addition of CH$_3$Si(Cl)$_2$H to tetrafluoroethylene in several experiments are plotted in Fig. 4. This clearly demonstrates the formation of the telomer CH$_3$Si(Cl)$_2$CF$_2$CF$_2$CF$_2$CF$_2$H.

Addition of silanes to olefins and acetylene in presence of chloroplatinic acid. Conditions and results of some experiments are set forth in Table 6. The catalyst was a 0.1 M solution of H$_2$PtCl$_6$·6H$_2$O in isopropyl alcohol.

We have to thank N. S. Andreev for taking the spectra of silanes.

SUMMARY

1. In the competing addition of silanes to ethylene in presence of H$_2$PtCl$_6$ the activity of the silanes is determined both by the inductive effect and the steric effect of the silyl groups, but the influence of the steric factor is greater than when the catalyst is platinum on a support.

2. Substituents have a deactivating influence on the ability of the double bond of an unsaturated compound to add on silanes in presence of H$_2$PtCl$_6$ and supported Pt. This is evidently also associated with the steric and inductive influence of these substituents.
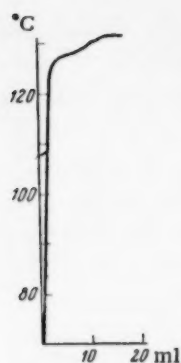
Fig. 2. Fractional
distillation curve
of product of addi-
tion of CH_3SiHCl_2
to $CF_2=CF(Cl)$ at
754.3 mm.

Fig. 3. Fractional
distillation curve
of products of telo-
merization of CF_2
$=CF(Cl)$ with
CH_3SiHCl_2 at atmo-
spheric pressure after
distillation in vacuo
(40-180° at 10-1 mm).
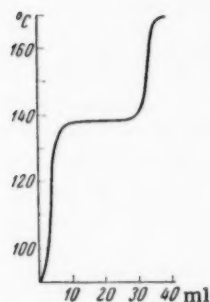
Fig. 4. Curve of frac-
tional distillation at
747.2 mm of 70 g of
products of telomeri-
zation of $CF_2=CF_2$
with $CH_3SiHHCl_2$
after distillation in
vacuo (30-150° at
8 mm).

3. The facts now known about the addition of silanes to unsaturated
compounds in presence of both H_2PtCl_6 and supported Pt are better explained
by the assumption of a specific radical mechanism rather than an ionic reac-
tion mechanism. The specificity of this process is associated with the role
of the catalyst surface or of complex-forming forces.

4. On the basis of the addition of silanes to unsaturated compounds in
presence of H_2PtCl_6 and supported Pt, a convenient and high-yielding method
of synthesis of a series of silicoorganic compounds of practical importance
was developed.

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RADIATION CHEMICAL CONVERSIONS OF ORGANIC SUBSTANCES

COMMUNICATION 4. OXIDATION OF ETHYLENE BY OXYGEN UNDER THE ACTION OF FAST ELECTRONS

B. M. Mikhailov and V. G. Kiselev

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

The study of the radiation chemical oxidation of unsaturated hydrocarbons by oxygen is of considerable interest. The possibility of carrying out the radiolysis at any temperature, in particular, at room and lower temperatures, makes it possible to isolate from the oxidation products unstable intermediate compounds, which is usually impossible in the study of thermal oxidation processes. Despite the great difference in the conditions, results obtained in the radiation chemical oxidation of lower olefins apparently can shed some light on the mechanism of thermal oxidation, which has not been elucidated up to now.

Very little work has been done on the oxidation of lower olefins under the action of radiation. There are only three communications on the radiolysis of water containing a dissolved mixture of ethylene and oxygen. Henley et al. [1,2] established that in this case, ethanol, acid, hydrogen peroxide, organic peroxide, and aldehydes are formed and according to the data of the authors, acetaldehyde was obtained in a yield of 60 molecules/100 ev. However, in the work of Clay, Johnson, and Weiss [3] it was stated that acetaldehyde is formed in considerably lower yields and that the only reaction products are formaldehyde, acetaldehyde, glycolaldehyde, and peroxides.

We studied the oxidation of ethylene by oxygen in the gas phase under the action of a beam of fast electrons. The effect of irradiation time, the ratio of the initial gases, the temperature, and the material of the reaction vessel was studied. We established the qualitative composition of the reaction products and carried out a quantitative analysis of both liquid and gaseous oxidation products and this made it possible to draw up a balance of carbon and oxygen between the starting gases and the reaction products.

Experiments on the effect of the total dose on the oxidation were carried out with ethylene−oxygen mixtures in a ratio of 1:1 in an aluminum chamber at room temperature and an initial pressure equal to atmospheric. The irradiation time was varied over the range 5 to 45 min (dose $0.2 \cdot 10^{23}$–$1.7 \cdot 10^{23}$ ev, respectively).

The results of the experiments, which are given in Figs. 1-4, show that over the dose range studied, ethylene reacts at a higher rate than oxygen and this difference increases considerably with a reduction in the total dose. This phenomenon is explained by an increase in the yield of acetylene and carbon monoxide in the initial period of the reaction and at first glance, it seems surprising as carbon monoxide is regarded as a secondary product in oxidation processes and its yield should fall with a decrease in exposure. In the given case, the increase in the carbon monoxide and acetylene yield at low doses may be explained by the catalytic effect of the chamber walls: in the initial period of radiation there is dehydrogenation of active molecules and primary peroxide products on the walls of the chamber which are covered with aluminum oxide, so that the reaction is displaced toward the formation of acetylene, carbon monoxide, and hydrogen with an increase in the ethylene consumption; however, after some time, the walls of the chamber are covered with a layer of liquid oxidation products and the catalytic effect of the walls is reduced to a considerable extent.
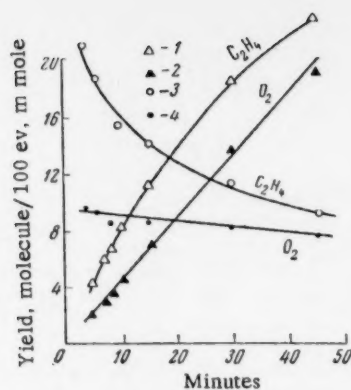
Fig. 1. Relation of decomposition and radiation chemical yields of ethylene and oxygen to irradiation time: 1,2) Decomposition; 3,4) yield per 100 ev.

Fig. 2. Relation of radiation chemical yields of oxidation products to irradiation time: 1) CH_3COOH; 2) CO_2; 3) CH_3CHO; 4) ROOR; 5) HCOOH; 6) C_2H_2; 7) H_2; 8) CO; 9) $HOCH_2CHO$.

Fig. 3. Relation of yields of oxidation products on ethylene reacting (on carbon) to irradiation time: 1) CH_3COOH; 2) CO_2; 3) CH_3CHO; 4) ROOR; 5) HCOOH; 6) C_2H_2; 7) H; 8) CO; 9) $HOCH_2CHO$.
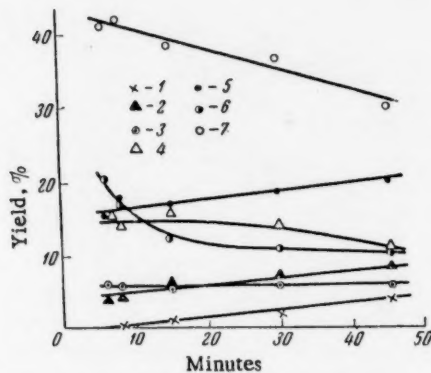
Fig. 4. Relation of yields of oxidation products on oxygen reacting to irradiation time: 1) CH_3COOH; 2)CO_2; 3) CH_3CHO; 4) ROOR; 5) HCOOH; 6) CO; 7) $HOCH_2CHO$.

This argument was confirmed by the following experiment: the starting mixture was irradiated for 4 min and after gas had been taken for analysis, mixture was introduced into the chamber up to atmospheric pressure and irradiation continued for a further 20 min; the gas was then completely removed from the chamber and the latter filled with fresh starting mixture, which was irradiated for 4 min. Gas analysis showed that less acetylene and considerably less carbon monoxide was formed in the second 4-min experiment than in the first.

The data presented show that the main oxidation products were glycolaldehyde, formic acid, carbon monoxide, acetylene and organic peroxides (hydrogen peroxide was formed in an insignificant yield)*. Formaldehyde was formed in a yield of 0.15 molecules/100 ev. After a reaction period of approximately 15 min, there was no sharp change in the relation of the yields of oxidation products to the total dose.

The relation of the oxidation process to the ratio of the starting gases was investigated in the same chamber at room temperature and an initial pressure equal to atmospheric and with an exposure of 15 min (dose $0.55 \cdot 10^{23}$ ev). The data presented in Fig. 5-8 show that the rates of the reaction of ethylene and oxygen depended strongly

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* ROOR denotes the sum of the peroxides in all graphs and tables.
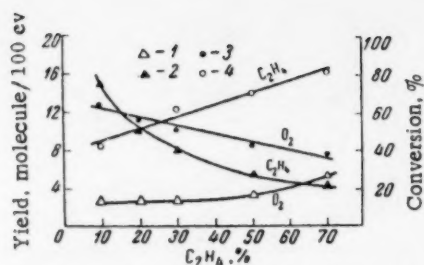
Fig. 5. Relation of conversion and radiation chemical yields of ethylene and oxygen to the composition of the starting mixture: 1,2) Conversion; 3,4) yield per 100 ev.

Fig. 6. Relation of radiation chemical yields of oxidation products to the composition of the starting mixture: 1) CO_2; 2) CH_3CHO; 3) ROOR; 4) HCOOH; 5) C_2H_2; 6) H_2; 7) CO; 8) $HOCH_2CHO$.

Fig. 7. Relation of yields of oxidation products on ethylene reacting (on carbon) to the composition of the starting mixture: 1) CO_2; 2) CH_3CHO; 3) ROOR; 4) HCOOH; 5) C_2H_2; 6) H_2; 7) CO; 8) $HOCH_2CHO$.
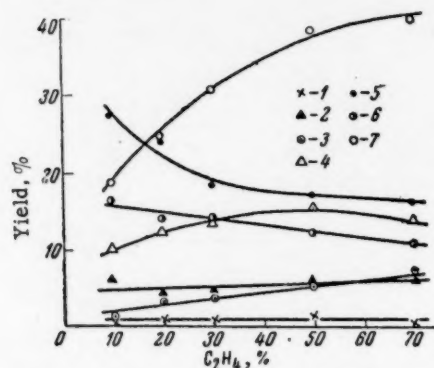
Fig. 8. Relation of the yields of oxidations products on the oxygen reacting to the composition of the starting mixture: 1) CH_3COOH; 2) CO_2; 3) CH_3CHO; 4) ROOR; 5) HCOOH; 6) CO; 7) $HOCH_2CHO$.

on the ratio of the gases in the starting mixture and this relation was expressed more strongly for ethylene. The experimental results show that a decrease in the ethylene content of the starting mixture led to almost complete oxidation of the ethylene taken and, on the other hand, an increase in the ethylene content increased the oxygen conversion, though the reverse relation was observed for the radiation chemical yields. It should be noted that with a decrease in the oxygen concentration in the starting mixture, processes which are not connected directly with the oxidation of ethylene began to play an increasing role. Thus, with an ethylene content of 70% in the starting mixture, only 45% of the carbon reacting was found in the oxygen-containing reaction products, while in the radiolysis of a mixture containing 20% ethylene, the oxygen-containing oxidation products contained 84% of the carbon reacting. Acetylene and butene were not formed when the starting mixture contained 10% of ethylene.

The data presented show that at low ethylene concentrations the main reaction products were formic acid and carbon monoxide, i.e., products from more extensive oxidation of ethylene. It should be noted that the energy yield of peroxides also depended little on both the ratio of the starting components and the dose. Formaldehydes was formed in a yield of 0.15-0.3 molecule/100 ev.

To determine the effect of the material of the chamber on the oxidation of ethylene under the action of fast electrons, we carried out experiments in glass, steel, and brass chambers. The results of the experiments are given in Table 1. These data show that the oxidation of ethylene (at a ratio of 1:1) is approximately the same in glass, steel, and aluminum chambers at room temperature with an exposure of 15 min (dose $0.55 \cdot 10^{23}$ ev). In the brass chamber there was a sharp fall in the yield of peroxides and glycolaldehyde and an increase in the yield of higher acids, carbon dioxide, formaldehyde, and butene. The fact that the ethylene and oxygen consumption was approximately the same in all chambers indicates that brass has a catalytic effect on the primary oxidation products, changing the direction of secondary reactions. It is evident that in this case products were formed which were found in an aluminum chamber as less than 75% of the oxygen reacting was found in the oxidation products, while in the other experiments the oxygen balance was close to 100%.

TABLE 1

Relation of Ethylene Oxidation to Material of Reaction Chamber

Material	Aluminum			Steel			Glass			Brass		
	C	O	G	C	O	G	C	O	G	C	O	G
C_2H_4	27,5		14,0	29,1		14,6	30,5		14,1	29,8		14,0
O_2		17,5	8,9		18,7	9,4		17,0	9,6		19,5	10,3
$HOCH_2CHO$	24,6	38,0	3,45	21,5	33,4	3,2	22,5	36,5	3,5	8,4	11,6	1,2
CH_3CHO	6,7	5,3	0,9	9,1	7,1	1,4	6,6	5,7	1,2	4,8	3,3	0,7
CH_2O	0,5	0,8	0,15	0,8	1,3	0,25	0,7	1,2	0,3	1,5	2,0	0,4
HCOOH	5,5	17,5	1,55	8,0	23,8	2,5	6,5	21,3	2,0	8,0	22,0	2,25
Peroxides	10,1	16,0	1,40	13,6	21,1	2,0	11,0	19,1	1,75	2,0	2,7	0,25
CO	9,2	12,8	2,6	7,2	11,1	2,0	9,3	15,1	2,8	9,6	12,2	2,6
CO_2	2,0	6,5	0,6	1,6	5,1	0,5	1,8	6,2	0,7	3,4	9,3	1,0
C_2H_2	11,0		1,55	14,1		2,0	13,9		2,0	12,9		1,80
C_4H_8	2,3		0,2	3,4		0,3	6,8		0,5	12,3		0,9
H_2	7,9		2,2	8,1		2,3	7,3		2,2	7,0		2,0
CH_3COOH	1,3	2,0	0,2	0	0	0	0	0	0	6,7	9,2	0,95

Note: C—yield on carbon; O—yield on oxygen; G—yield per 100 ev.

TABLE 2

Temperature Dependence of Radiation Chemical Yields (aluminum chamber)

Temp. °C	$\begin{matrix}CH_2OH \\ | \\ CHO\end{matrix}$	CH_3CHO	CH_2O	HCOOH	ROOR	CO	CO_2	C_2H_2	H_2
—40	3,75	0,9	0,3	1,55	2,4	2,5	0,3	1,75	2,4
0	3,40	0,9	0,35	1,55	2,05	2,35	0,3	1,60	2,4
20	3,45	0,9	0,15	1,55	1,40	2,6	0,6	1,55	2,2
80	3,45	1,0	0,25	2,0	1,15	3,5	1,1	2,0	1,2

TABLE 3

Temperature Dependence of Radiation Chemical Yields (glass chamber)

Temp. °C	$\begin{matrix}CH_2OH \\ | \\ CHO\end{matrix}$	CH_3CHO	CH_2O	HCOOH	ROOR	CO	CO_2	C_2H_2	H_2
—40	2,95	0,8	0,35	1,95	2,40	2,9	0,35	1,6	2,0
0	3,30	0,9	0,25	1,95	1,95	2,5	0,3	1,6	2,0
20	3,50	1,2	0,30	2,0	1,75	2,8	0,7	2,0	2,2

The effect of temperature on ethylene oxidation was studied with 1:1 mixtures in an aluminum chamber over the temperature range of -40 to +80° and in a glass chamber over the range of -40 to +20° with a 15-min exposure. The results of these experiments are given in Tables 2 and 3.

Tables 2 and 3 show that with a change in temperature from -40 to +20°, in an aluminum chamber there was hardly any change in the yields of the main products with the exception of peroxides whose yield increased appreciably with a fall in temperature. In a glass chamber the temperature dependence of the yields was more appreciable, but in this case also there were no considerable changes in the yields of the main products. The increase in the peroxide yield is apparently explained by their stabilization at lower temperatures and also by their more rapid removal from the reaction sphere. At 80° there was an appreciable increase in the yield of formic acid, carbon monoxide, acetylene, and carbon dioxide together with a fall in the yield of peroxides and hydrogen and this was apparently connected with slow deposition of the reaction products on the walls of the chamber, leading to the catalytic effect mentioned above, and also an increase in the role of secondary reactions. In general, the data presented indicates that the oxidation of ethylene and the action of fast electrons depends little on temperature.

DISCUSSION OF EXPERIMENTAL RESULTS

The combination of facts presented makes it possible to draw some conclusions on the mechanism of radiolytic oxidation of ethylene. It is quite evident that the oxidation of ethylene proceeds mainly through the formation and subsequent conversions of organic peroxides. This conclusion follows from the fact that the yield and concentration of peroxides in the reaction chamber during an experiment depends little on the total dose and the composition of the starting mixture and is confirmed by the increase in the peroxide yield with a fall in the temperature of the reaction medium. We feel sure that the primary act of excitation and ionization of an ethylene molecule results in the formation of a molecular peroxide with the structure $\begin{matrix} CH_2-CH_2 \\ | \quad\quad | \\ O-O \end{matrix}$. The formation of this peroxide

is best confirmed by the formation of glycolaldehyde, which may result from isomerization of this peroxide. The possibility of the formation of cyclic peroxides by oxidation of a double bond has been reported by various authors [4,5]. In the opinion of Medvedev [6], the formation of ethylene peroxide with the composition $C_2H_4O_2$ is most probable in the oxidation of ethylene; this hypothesis is also supported by other investigators [7]. This cyclic peroxide of ethylene may evidently exist in the form of the biradical $\begin{matrix} OH \quad OH \\ | \quad\quad | \\ -CH-CH- \end{matrix}$ [8] and, by adding an oxygen molecule, be oxidized to a peroxide with the structure of dihydroxyethylene peroxide $\begin{matrix} O-O \\ | \quad\quad | \\ CH-CH \\ | \quad\quad | \\ OH \quad OH \end{matrix}$ or the isomeric peroxide
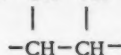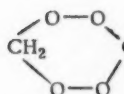
$\begin{matrix} \quad O-O \\ CH_2 \quad\quad CH_2 \\ \quad O-O \end{matrix}$, which is the dimer of methylene peroxide. It is known that alkylidine peroxides are readily con-

verted to the isomeric acids [9] and in our experiments, formic acid is probably formed by precisely this route. Experiments showed that the formic acid content of the reaction products increased after alkaline decomposition of the peroxides; consequently, it may be assumed that the oxidation products contained one of these peroxides. Formic acid was not formed from dihydroxymethyl peroxide [10] in the given case as dihydroxymethyl peroxide was not detected in our experiments. Likewise, it is evident that formic acid was not formed by oxidation of formaldehyde as it is unreasonable to assume that formaldehyde was oxidized almost quantitatively, while acetaldehyde and glycolaldehyde were hardly oxidized under the same conditions. Acetaldehyde was evidently formed by the reaction of the peroxide $C_2H_4O_2$ with ethylene to form two $-CH_2-CH_2-O$ radicals, which underwent isomerization. Lenher [10] explained the formation of ethylene oxide during the thermal oxidation of ethylene in this way. Formaldehyde was evidently formed by rupture of an ethylene peroxide molecule. This reaction should be regarded as a side reaction as formaldehyde was formed in low yield in all experiments.

The greatest difficulty in the elucidation of the reaction mechanism was caused by the formation of large amounts of carbon monoxide during the radiolytic oxidation of ethylene. The temperature independence of the carbon monoxide yield and also the considerable increase in its yield in the initial reaction period compels us to assume that carbon monoxide was formed largely not from formic acid, as is generally considered, but by complete oxidation of the ethylene molecule, though the mechanism of this process is not clear.

The quite high yield of acetylene in our experiments should be mentioned. This yield almost equalled the acetylene yield calculated on carbon in the radiolysis of pure ethylene, which we investigated [11], and we observed an analogous relation to total dose. Thus, the dehydrogenation of ethylene both in the radiolysis of pure ethylene and in the radiolysis of mixtures of it with oxygen at not too high concentrations of the latter proceeds independently of the other processes. As the data presented show, the radiation chemical yield of ethylene oxidation depends on the total dose and the ratio of the starting components and for a 15-min experiment with a 1:1 starting mixture, it equals 14 molecules of ethylene per 100 ev of absorbed energy, which, in combination with the low temperature dependence, indicates that the radiolytic oxidation of ethylene is a nonchain process. Thus, the proposed mechanism for ethylene oxidation consists essentially of the formation of ethylene peroxide and its subsequent conversions by isomerization and reactions with oxygen and ethylene, leading to the main final oxidation products according to the following scheme:

$$C_2H_4 \longrightarrow \cdot \wedge \wedge \wedge \rightarrow C_2H_4{}^+$$

$$C_2H_4{}^+ \xrightarrow{O_2} C_2H_4O_2$$

$$C_2H_4O_2 \longrightarrow HOCH_2CHO$$

$$C_2H_4O_2 \xrightarrow{O_2} 2HCOOH$$

$$C_2H_4O_2 \xrightarrow{C_2H_4} 2CH_3CHO$$

$$C_2H_4{}^+ + O_2 \longrightarrow 2CO + 2H_2$$

$$C_2H_4{}^+ + 2O_2 \longrightarrow 2CO + 2H_2O$$
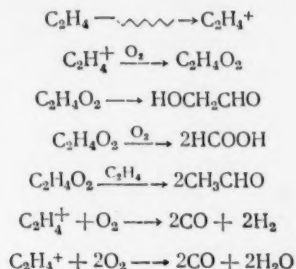
The material presented shows that the radiolytic oxidation of ethylene differs substantially with respect to the composition and yields of the products from thermal oxidation, but the latter apparently must also proceed through the formation of primary peroxide compounds, as is assumed by a number of investigators.

EXPERIMENTAL

The irradiation was carried out in 2-liter aluminum, glass, steel, and brass chambers with an accelerating field of 115 kv and a current strength of 0.1 ma. At the end of an experiment, the chamber was cooled with iced water (a loss up to 10% of the products obtained in the form of vapor was possible at room temperature). Gas was removed from the cooled chamber with an evacuated pipette for analysis; the products were washed from the walls of the chamber with four 25-30 ml portions of water. The solution obtained in this way was used for analyses.

The liquid reaction products consisted of a light yellow, quite mobile oil, which was almost completely soluble in water and had the sharp odor characteristic of peroxides. Only aqueous solutions were used for analysis.

Carbonyl compounds. The aldehydes were precipitated from solution as the 2,4-dinitrophenylhydrazones and the mixture of these was extracted with hot alcohol to yield a substance, which gave the red color with alcoholic alkali that is characteristic of hydrazones, but did not correspond to any individual hydrazone as regards melting point. Repeated recrystallization from alcohol did not give a positive result. The substance was purified by chromatography on alumina (deposited as a benzene solution and eluted with a 4% solution of butanol in n-hexane) and was found to be acetaldehyde 2,4-dinitrophenylhydrazone with m.p. 160-162°. Found: C 43.18; H 3.65; N 25.19%; molecular weight 220. $C_8H_8N_4O_4$. Calculated: C 42.87; H 3.59; N 25.0%; molecular weight 224.

From the mother solution we isolated crystals which were identical with the main fraction, but somewhat worse as regards melting point. We also found traces of a hydrazone of undetermined structure. The residue after alcohol extraction contained dinitrophenylosazones (blue color with alcoholic alkali) and was recrystallized repeatedly from pyridine. The main fraction of crystals isolated had m.p. 318° (with decomposition), which corresponds to the melting point of glyoxal 2,4-dinitrophenylosazone (314-320°, according to the data of various authors). Purification of the osazone fraction by chromatography on alumina (the substance was deposited in benzene and eluted with pyridine or ethyl acetate) with subsequent recrystallization from pyridine yielded an osazone with m.p. 320.5° (with decomposition). The elementary analysis corresponded to glyoxal dinitrophenylosazone. Found: C 40.50; H 2.40%. $C_{14}H_{10}N_8O_8$. Calculated: C 40.20; H 2.40%.

However, the solution containing the oxidation products of ethylene did not give a positive reaction for glyoxal and likewise, no oxalic acid was obtained when the solution was treated with hydrogen peroxide in an alkali medium. There facts indicate that the radiolytic oxidation of ethylene under normal conditions yielded not glyoxal, but glycolaldehyde as the latter gives only glyoxal osazone on reaction with 2,4-dinitrophenylhydrazine and the literature contains no information on the preparation of glycolaldehyde dinitrophenylhydrazone. Formaldehyde hydrazone was not found, but the solution of the reaction products gave a positive reaction with phenylhydrazine and potassium ferricyanide, indicating the presence of formaldehyde in very small amounts. Thus, the carbonyl compounds obtained in the radiolytic oxidation of ethylene consisted almost solely of glycolaldehyde and acetaldehyde (at an ethylene—oxygen ratio in the starting mixture of 1:1).

Acids. The analysis solution was concentrated and extracted with ether. Removal of the ether yielded a small amount of a dark liquid with a strong odor of formic acid. The presence of the latter was demonstrated by the formation of a precipitate of aniline formate and the liberation of carbon monoxide when the liquid was heated with concentrated sulfuric acid. Traces of an involatile acid of undetermined structure were found by means of paper chromatography. Thus, the difference between the total acidity and the formic acid is explained by the presence of acetic acid.

Peroxides. The reaction with titanium—sulfuric acid showed that hydrogen peroxide was formed in a very low yield, but the oxidation products contained organic peroxides, which reacted slowly with titanium—sulfuric acid. These peroxides were comparatively stable: the peroxide content hardly changed when the analysis solution was kept at room temperature for 8 hr and only half of the peroxide was destroyed when the solution was boiled for 30 min. However, the peroxides disappeared completely when a neutralized solution containing 0.05-0.1% of NaOH was heated at 70-80° for 4 min and then the alkalinity of the solution decreased by a value which almost equalled the peroxide content, i.e., there was isomerization or decomposition of peroxides to form carboxylic acids. At room temperature, 75% of the peroxides were decomposed in 1 hr. It was established that the acids (bulk) and formic acids, and involatile acids and CO_2 were not found. On the other hand, determination of the amount of peroxides by the iodine method showed that the peroxides reacted differently with a neutral solution of potassium iodide, depending on the oxidation conditions. Thus, it may be considered that the reaction products contained at least two types of organic peroxides, which were not normal hydroperoxides or dialkyl peroxides. Ethylene oxide was not found in the reaction products.

Quantitative analysis procedure. The total acids were determined by titration of an aliquot portion of the solution with 0.1 N NaOH solution. The total peroxides were determined by the iodine method. The total aldehydes were determined by oxidation with excess hydrogen peroxide in an alkaline medium to the corresponding acids [12]. The peroxides in the solution for the determination were destroyed by the addition of 0.1 N NaOH (3-5 ml per 10 ml of neutral solution) and heating the solution at 75-80° for 4 min with subsequent neutralization. For the determination of formic acid, an aliquot portion of the solution was boiled with a solution of mercuric acetate (II) and the carbondioxide liberated determined in a special absorber [13]. It was first established that formaldehyde did not appreciable increase the error of the determination. The acetaldehyde was determined by distillation from the boiling solution in a slow stream of air for 20 min in the apparatus used for the determination of formic acid. The aldehyde vapor was absorbed in hydroxylamine solution. By this method we determined 97-98% of the theoretical amount of aldehyde. Formaldehyde was determined colorimetrically from the formation of a red color on treatment of the solution with phenylhydrazine and potassium ferricyanide in the presence of concentrated hydrochloric acid [14]. Glycolaldehyde was determined from the difference between the total aldehydes and the sum of formaldehyde and acetaldehyde. The satisfactory agreement of the balances showed that this method gave acceptable results. The gas mixtures were analyzed on a No. 4 chromathermograph and on a VTI-2 apparatus.

We would like to thank V. S. Bogdanov for help in this investigation.

SUMMARY

1. The oxidation of ethylene by oxygen under the action of fast electrons was investigated. The effect of the total radiation dose, temperature, material of the reaction vessel, and ratio of the starting gases on the oxidation was determined.

2. During radiolytic oxidation, ethylene is converted mainly into glycolaldehyde, formic acid, organic peroxides, carbon monoxide, and acetylene. The reaction depends little on temperature. The oxidation of ethylene is approximately the same in glass, aluminum, and steel, but the nature of the reaction changes appreciably in a brass chamber.

3. It was established that the wall of the reaction chamber has a catalytic effect on the oxidation of ethylene in the initial stages of the reaction.

4. The temperature independence of the reaction and the comparatively low energy yield indicate that the radiolytic oxidation of ethylene is a nonchain process.

5. A reaction mechanism based on the formation and subsequent conversions of ethylene peroxide is proposed.

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SYNTHESIS OF PYRIDINE BASES FROM VINYLACETYLENE

COMMUNICATION 4. CONDENSATION OF SECONDARY VINYLETHYNYLCARBINOLS WITH AMMONIA

I. L. Kotlyarevskii and L. I. Vereshchagin

Institute of Chemistry, Eastern Siberian Branch of the Academy of Sciences, USSR

As we showed on a series of examples [1], tertiary vinylethynylcarbinols undergo a catalytic reaction with ammonia to form pyridine bases. To determine the limits of applicability of this reaction, in the present work we studied the catalytic condensation of ammonia with two secondary vinylacetylenic alcohols, namely, methylvinylethynylcarbinol and ethylvinylethynylcarbinol. It was found that these carbinols react with ammonia over the catalysts $CdHPO_4/CaHPO_4$ (20:80) and CdO/Al_2O_3 (30:70) at 285-470° to form pyridine bases. Thus, methylvinylethynylcarbinol and ammonia gave a total yield of 17.3% of a mixture of 2- and 4-picolines and 2,4-lutidine, while the main pyridine base obtained from ethylvinylethynylcarbinol was 2-ethyl-3,5-dimethylpyridine. The neutral part of the catalyzate was found to contain propionitrile, whose formation may be explained only by the presence of propionaldehyde in the reaction mixture; the formation of aldehydes and nitriles from them is explained by decomposition of the starting carbinols at high temperature [2].

In connection with this we carried out the catalytic synthesis of the above pyridine bases both from a mixture of aldehyde, vinylacetylene, and ammonia and also from aldehydes and ammonia. In both cases, in addition to the corresponding nitriles, we obtained the same pyridine bases, but in higher yield than from the carbinols. The yields of the pyridine bases obtained from aldehydes and ammonia in the presence of vinylacetylene were the same as those obtained in the absence of vinylacetylene and from this we can conclude that the vinylacetylene did not participate in the reaction in the given case and the pyridine bases were formed by the Chichibabin reaction.
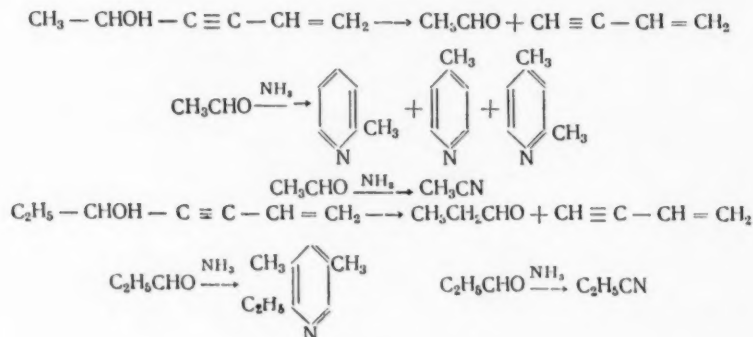
EXPERIMENTAL

As in the case of tertiary carbinols, the catalytic conversions of the secondary vinylethynylcarbinols were carried out by passing them simultaneously with ammonia over 40 ml of catalyst at 390-400° and a space velocity of 1.0-1.2 hr^{-1}. The bases were isolated by treatment of the catalyzate with hydrochloric acid and subsequent neutralization. The pyridine bases which had been accumulated under definite conditions were distilled on a column of 25 theoretical plates. The method of preparing the catalysts was given in a previous paper [1]. The vinylethynylcarbinols were obtained by Iotsich's method from vinylacetylene and aldehydes. Methylvinylethynyl-carbionol had b.p. 64° (18 mm); n_D^{15} 1.4870. Ethylvinylethynylcarbinol had b.p. 65-70° (9 mm); n_D^{15} 1.4845. Vinylacetylene was obtained by decomposition of dimethylvinylethynylcarbinol with potassium hydroxide at 100°.

The catalytic treatment of methylvinylethynylcarbinol with ammonia was carried out on $CdHPO_4/CaHPO_4$ at 390° with a carbinol space velocity of 1.0 hr^{-1} and a molar ratio of carbinol to ammonia of 1:3. Under these conditions, we obtained 2.3 g of bases from 14.2 g of carbinol. We accumulated 38.4 g of bases in this way and distilled them on a column to obtain the following fractions: fraction I with b.p. 127.5-128.5° (730 mm); 13.7 g; n_D^{17} 1.5019 (picrate, m.p. 169°; chloroplatinate, m.p. 193.5-194°; chloromercurate, m.p. 153°), was α-picoline. Fraction II with b.p. 143-144° (730 mm); 4.8 g; n_D^{17} 1.5050 (picrate, m.p. 166-166.5°; chloroplatinate, m.p. 240-243°; chloromercurate, m.p. 128°; iodomethylate, m.p. 226°), was γ-picoline. Fraction III with b.p. 157-159° (730 mm); 1.6 g; n_D^{20} 1.5033 (picrate, m.p. 181°; chloroplatinate, m.p. 210-212°), was 2,4-lutidine. The constants of the pyridine bases obtained agreed with literature data [3].

The reaction of ammonia and 21 g of paraldehyde, which was introduced at a rate of 1.4 hr^{-1}, under the same conditions yielded 20 g of catalyzate, from which we isolated 7.0 g of bases. Distillation of 35 g of bases obtained under these conditions yielded the following main fractions: fraction I with b.p. 125-135°, 14.6 g; picrate m.p. 166-169°. Fraction II with b.p. 140-150°; 5.3 g; picrate, m.p. 166-167°. Fraction III with b.p. 155-165°; 0.9 g; picrate, m.p. 166-167°. Fraction III with b.p. 155-165°; 0.9 g; picrate, m.p. 181°. Fractions I, II, and III were α- and γ-picolines and 2,4-lutidine, respectively. The picrates of these compounds did not depress the melting points of the picrates of the same pyridine bases obtained agreed with literature data [3].

The reaction of ammonia and 21 g of paraldehyde, which was introduced at a rate of 1.4 hr^{-1}, under the same conditions yielded 20 g of catalyzate, from which we isolated 7.0 g of bases. Distillation of 35 g of bases obtained under these conditions yielded the following main fractions: fraction I with b.p. 125-135°, 14.6; picrate, m.p. 167-169°. Fraction II with b.p. 140-150°; 5.3 g; picrate, m.p. 166-167°. Fraction III with b.p. 155-165°; 0.9 g; picrate, m.p. 181°. Fractions I, II, and III were α- and γ-picolines and 2,4-lutidine, respectively. The picrates of these compounds did not depress the melting points of the same pyridine bases obtained from methylvinylethynylcarbinol. From the neutral part of the catalyzate we distilled 1.6 g of acetonitrile with b.p. 80-85°; n_D^{20} 1.3445.

Catalytic treatment of 20 g of paraldehyde and 8 g of vinylacetylene with ammonia under the same conditions as for paraldehyde and ammonia yielded 7.3 g of bases, which were fractionated to yield 2.9 g of a fraction with b.p. 125-135°; picrate, m.p. 167-169° (α-picoline); 1.3 g of a fraction with b.p. 140-150°; picrate, m.p. 166-167° (γ-picoline), and 0.200 g of a fraction with b.p. 155-165°; picrate, m.p. 181° (2,4-lutidine). The picrates of the pyridine bases obtained did not depress the melting points of authentic samples. By distillation of the neutral part of the catalyzate we isolated 1.5 g of acetonitrile.

The catalytic treatment of ethylvinylethynylcarbinol with ammonia was carried out over $CdHPO_4/CaHPO_4$ at 400° with a carbinol space velocity of 1.2 hr^{-1} and a molar ratio of carbinol to ammonia of 1:3. In this way we obtained 2.5 g of bases from 11 g of ethylvinylethynylcarbinol. Distillation of 25.5 g of these bases on a column yielded 32% of a main fraction with b.p. 190-195° (725 mm) (picrate, m.p. 151-152°), which was 2-ethyl-3,5-dimethylpyridine. According to literature data [3]: b.p. 198° (764 mm); picrate, m.p. 152°. From the neutral part of the catalyzate we isolated 0.8 g of propionitrile with b.p. 94-100° and n_D^{20} 1.3683. Catalytic treatment of 28 g of propionaldehyde (b.p. 48°; n_D^{20} 1.3640) with ammonia under the same conditions gave 8.1 g of bases, fractionation of which yielded 62.0% of a fraction with b.p. 190-195° (725 mm) (picrate, m.p. 151-152°), which was 2-ethyl-3,5-dimethylpyridine. The picrate did not depress the melting point of the picrate of 2-ethyl-3,5-dimethylpyridine obtained from ethylvinylethynylcarbinol. From the neutral reaction products we isolated 1.4 g of propionitrile with b.p. 94-100° and n_D^{20} 1.3684.

A mixture of 13 g of propionaldehyde and 4 g of vinylacetylene was passed over $CD_3(PO_4)_2/Al_2O_3$ at a rate of 1.4 hr^{-1}. Ammonia was introduced at a rate of 30 liter/hr. We obtained 3.4 g of bases. Distillation of the latter

yielded 60.7% of 2-ethyl-3,5-dimethylpyridine with b.p. 190-198° (735 mm) (picrate, m.p. 152°). A mixed melting point with picrates of authentic samples was not depressed. From the neutral reaction products we isolated 0.6 g of propionitrile.

SUMMARY

During condensation with ammonia over cadmium catalysts at 400°, a secondary vinylethynylcarbinols are decomposed to aldehydes and vinylacetylene. Acetaldehyde formed in the process undergoes the Chichibabin reaction with ammonia to give α- and γ-picolines and 2,4-lutidine; propionaldehyde gives 2-ethyl-3,5-dimethylpyridine.

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SYNTHESIS OF PYRIDINE BASES FROM VINYLACETYLENE

COMMUNICATION 5. CONDENSATION OF KETONES WITH METHYL VINYL KETONE AND AMMONIA

L. I. Vereshchagin and I. L. Kotlyarevskii

Institute of Chemistry, Eastern Siberian Branch of the Academy of Sciences USSR

In previous work [1-4] we presented the results of investigating the preparation of pyridine bases by condensation of vinylethynylcarbinols with ammonia in the presence of hydrating catalysts. This formed a readily separable mixture of pyridine bases which consisted mainly of 2,6-disubstituted pyridines:

$$\underset{R}{\overset{CH_3}{>}}\underset{OH}{\overset{|}{C}} - C \equiv C - CH = CH_2 \xrightarrow{NH_3} CH_3 - \underset{N}{\bigcirc} - R$$
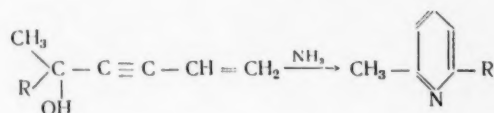
where R is alkyl or aryl.

This scheme was confirmed with dimethylvinylethynylcarbinol, methylethylvinylethynylcarbinol, and methylphenylvinylethynylcarbinol. When the same reaction was carried out with secondary vinylethynylcarbinols (methyl and ethylvinylethynylcarbinols), we observed deviations from the general reaction scheme [4]: firstly, aceto- and propionitriles were obtained and secondly, from ethylvinylethynylcarbinol we obtained 2-ethyl-3,5-dimethylpyridine, whose formation does not correspond to the general reaction scheme. This compelled us to assume that at the higher temperature required for these reactions, vinylethynylcarbinols decompose to the starting carbonyl compounds and vinyl acetylene, which can then react in different directions: a) in the case of tertiary carbinols, the ketone and vinylacetylene formed react with ammonia to give pyridine bases; b) in the case of secondary carbinols, the aldehydes formed by their decomposition give either nitriles or pyridine bases by the Chichibabin reaction.

This hypothesis was completely confirmed as the condensation of vinyl acetylene with ketones and ammonia yielded the same products as tertiary carbinols, but in a considerably higher yield [3,4]. Under the same conditions, but in the absence of vinyl acetylene, ketones and ammonia hardly gave any pyridine bases. The hypothesis was also confirmed by the fact that after hydrogenation to dimethylbutadienylcarbinol by LiAlH$_4$, dimethylvinylethynyl-carbinol did not form pyridine bases under the conditions used and this was apparently due to the fact that acetone and vinylacetylene could not be formed by its decomposition. It should be mentioned that the methyl ether of dimethylvinylethynylcarbinol does not give pyridines, evidently for the same reason .

The condensation of acetaldehyde or propionaldehyde with vinylacetylene and ammonia yielded the same pyridine bases as secondary carbinols, but in higher yield, though since the same yield of the same pyridines was obtained from aldehydes and ammonia in the absence of vinylacetylene, it must be assumed that the reaction here proceeded according to a Chichibabin scheme and the vinylacetylene did not participate in the reaction [4].

Acetylene is known to be hydrated to acetaldehyde on cadium catalysts and in 1958 a report appeared [5] that vinylacetylene is hydrated to methyl vinyl ketone over cadmium calcium phosphate, which we used as one of the catalysts for the formation of pyridine bases. In this connection, in determining the role of vinylacetylene in the synthesis of pyridines it was natural to assume its intermediate hydration to methyl vinyl ketone by water formed both by partial decomposition of the excess ketone introduced and in the formation of pyridine bases.

To check this hypothesis, in the present work we synthesized pyridine bases by condensation of a series of methyl ketones with methyl vinyl ketone and ammonia. This reaction was carried out over the catalyst $Cd_3(PO_4)_2$ /Al_2O_3 (20:80) at the optimal temperatures and space velocities found in the condensation of these ketones with vinylacetylene and ammonia. Both the methyl ketones and ammonia were taken in excess and in the same molar ratios as in the condensation with vinylacetylene [2,3]. We investigated the reaction of ammonia and methyl vinyl ketone with acetophenone, p-methylacetophenone, p-ethylacetophenone, pinacolin, acetone, and methyl ethyl ketone. In this way we obtained, respectively, 2-methyl-6-phenylpyridine ((I), R= C_6H_5), 2-methyl-6-(p-methyl-phenyl)pyrdine [(I), R = p-$CH_3C_6H_4$], 2 methyl-6-(p-ethylphenyl)pyridine [(I) R= p-$C_2H_5C_6H_4$], 2-methyl-6-tert-butylpyridine [(I), R=t-CH_4H_2], and from acetone, 2,6-dimethylpyridine (II) and 2,4-dimethylpyridine (III) and from methyl ethyl ketone, 2-methyl-6-ethylpyridine (IV) and 2,3,6-trimethylpyridine (V). The yields in these reactions differed little from those obtained in the reaction of methyl ketones with vinylacetylene and ammonia:

$$R-CO-CH_3 + CH_3-CO-CH=CH_2 \xrightarrow{NH_3} CH_3-[\text{(I)}]-R$$

(I)

where

$$R = C_6H_5-, \quad p\text{-}CH_3C_6H_4-, \quad p\text{-}C_2H_5C_6H_4-, \quad t\text{-}C_4H_9-$$

$$CH_3-CO-CH_3 + CH_2-CO-CH=CH_2 \xrightarrow{NH_3} CH_3-[\text{(II)}]-CH_3 + CH_3-[\text{(III)}]$$

(II)   (III)

$$C_2H_5-CO-CH_3 + CH_3-CO-CH=CH_2 \xrightarrow{NH_3} CH_3-[\text{(IV)}]-C_2H_5 + CH_3-[\text{(V)}]$$

(IV)   (V)
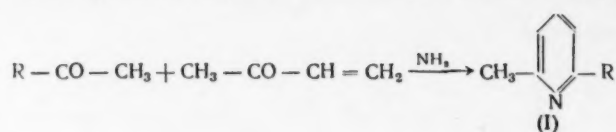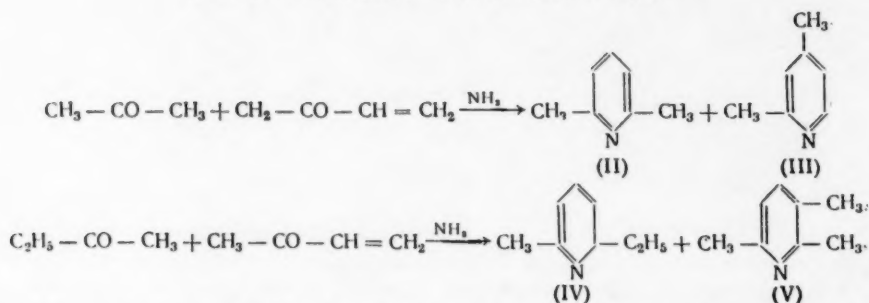
The structures of the compounds obtained were confirmed by mixed melting points of the picrates with picrates of authentic compounds.

Thus, on the basis of all that has been presented above, the mechanism of the formation of pyridines from vinylethynylcarbinols seems to be as follows: at the high experimental temperature, the vinylethynylcarbinols are cleaved over the catalysts to the starting methyl ketone and vinylacetylene and in the presence of the hydrating catalysts, the latter is hydrated to methyl vinyl ketone, which reacts with the methyl ketone and ammonia to form 2-methyl-6-R-pyridines as the main products.

$$\begin{array}{c} CH_3 \\ R \end{array}\!\!\!>\!C-C\equiv C-CH=CH_2 \longrightarrow \begin{array}{c} CH_3 \\ R \end{array}\!\!\!>\!CO + CH\equiv C-CH=CH_2$$
$$\underset{OH}{|}$$

$$CH\equiv C-CH=CH_2 + H_2O \xrightarrow{\text{catalyst}} CH_3-CO-CH=CH_2$$

$$R-CO \quad CO-CH_3 \quad \longrightarrow R-[\ ]-CH_3$$
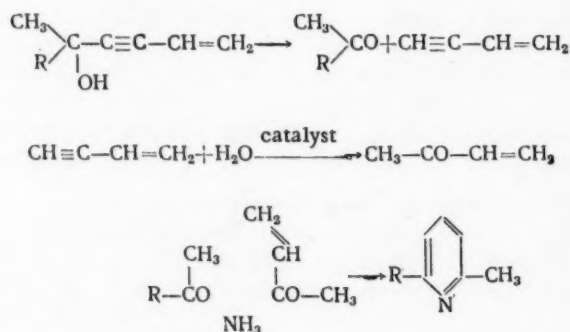
In the case of methyl ethyl ketone, 2,3,6-trimethylpyridine is formed in a higher yield than 2-methyl-6-ethylpyridine as a result of the lability of the hydrogen of the methylene group and this is superposed on the general scheme:
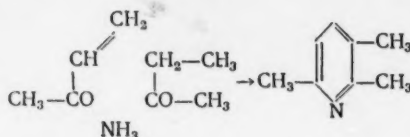
Ketones which do not contain labile hydrogen atoms in a position α to the carbonyl group do not form pyridine bases, as we demonstrated in the case of benzophenone.

For the latter stage of the reaction, namely, the formation of the pyridine nucleus from methyl ketones, methyl vinyl ketones, and ammonia, we may adopt the mechanism proposed by Weiss [6], who showed that substituted vinyl ketones react with acetophenone by a Michael addition to form 1,5-diketones [7]; the latter react with ammonia to give dihydropyridines, which are dehydrogenated to pyridines, donating the hydrogen molecule to excess vinyl ketone. The reaction of methyl vinyl ketone with acetoacetic ester and ammonia proceeds according to approximately the same scheme [8]. From this point of view, the last stage of our reaction may be represented in the following way:
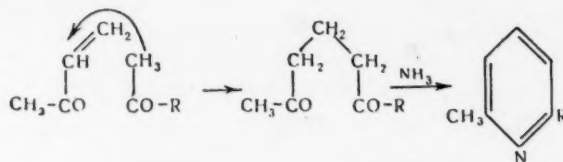
EXPERIMENTAL

The pyridine bases were synthesized from methyl ketones, methyl vinyl ketone, and ammonia over 40 ml of the catalyst $Cd_3(PO_4)_2/Al_2O_3$ in a quartz tube in a tubular furnace. Methyl vinyl ketone, stabilized with hydroquinone, was mixed in definite proportions with appropriate ketones. The mixture was introduced into the reaction at a space velocity of $1.4 \, hr^{-1}$ at 400°. The ammonia was introduced at a rate of 30 liter/hr. The method of treating the reaction products and isolating the bases was given in previous work.

Methyl vinyl ketone was synthesized by dehydration of acetoethanol with potassium bisulfate. The acetoethanol was obtained by Vul'fson's method [9]. For the dehydration, 84 g of acetoethanol and 1 g of finely ground potassium bisulfate was heated to boiling on Wood's metal, whereupon 25 g of methyl vinyl ketone distilled. After redistillation, the methyl vinyl ketone had b.p. 82-83°; n_D^{20} 1.4112.

Catalytic treatment of acetone and methyl vinyl ketone with ammonia. A mixture of 13.5 g (0.24 mole) of acetone and 5.6 g (0.08 mole) of methyl vinyl ketone was passed over the catalyst. We obtained 21 g of catalyzate, from which 4.8 g of bases was isolated. Under similar conditions we accumulated 38 g of bases, which were distilled on a column of 25 theoretical plates to yield the following fractions: fraction I, b.p. up to 134° (735 mm); 2.5 g; fraction II, b.p. 140-146° (735 mm); 17.6 g; picrate, m.p. 161-163°; fraction III, b.p. 146-150°; 3.0 g; fraction IV, b.p. 150-160° (735 mm); 5.2 g; picrate, m.p. 181°; fraction V, b.p. 160-168°; 1.6 g; fraction VI, b.p. 168-175°; 3.4 g; picrate, m.p. 154-156°.

Fraction II was 2,6-dimethylpyridine, fraction IV, 2,4-dimethylpyridine, and fraction VI, 2,4,6-trimethylpyridine. The melting points of the picrates of the bases obtained agreed with literature data [10] for the corresponding pyridines and did not depress the melting points of picrates of individual pyridine bases synthesized from acetone and vinylacetylene with ammonia.

The effect of reaction temperature and the molar ratio of methyl vinyl ketone and acetone on the yield of bases was studied; the data are given in the table.

Condensation of methyl ethyl ketone with methyl vinyl ketone and ammonia. Passing a mixture of 33 g (0.45 mole) of methyl ethyl ketone and 8 g (0.11 mole) of methyl vinyl ketone over the catalyst yielded 35.0 g

Expt. No.	Reaction temperature, °C	Molar ratio of methyl vinyl ketone to acetone*	Catalyzate yield, %	Yield of bases on methyl vinyl ketone, %
Effect of reaction temperature				
1	300	1:3	81.0	26.9
2	350	1:3	90.3	34.8
3	400	1:3	98.0	56.2
4	450	1:3	76.2	46.7
Effect of molar ratio or reagents				
5	400	1:1	75.4	13.8
6	400	1:3	98.0	56.2
7	400	1:6	97.4	58.3

* Ammonia input rate 30 liter/min.

of catalyzate, from which we isolated 8.4 g of bases. We accumulated 31.6 g of bases under these conditions and carefully distilled them from a Favorskii flask to yeild the following fractions: fraction I, b.p. up to 155° (730 mm); 0.8 g; fraction II, b.p. 155-165° (730 mm); 2.5 g; picrate m.p. 120-122°; fraction III, b.p. 165-175°; 13.6 g; picrate, m.p. 145-147°; fraction IV, b.p. 175-185° (730 mm); 5.8 g, and fraction V, b.p. 185-205° (730 mm); 5.0 g; picrate, m.p. 172-174°. Fractions II, III, and V were 2-methyl-6-ethylpyridine, 2,3,6-trimethylpyridine, and 2,3,5,6-tetramethylpyridine, respectively. The constants of the pyridine bases isolated agreed with literature data [10] and the picrates did not depress the melting points of picrates of individual samples obtained from methyl ethyl ketone and vinylacetylene with ammonia.

Catalytic treatment of pinacolin with methyl vinyl ketone and ammonia. A mixture of 25.5 g (0.25 mole) of pinacolin (b.p. 106°) and 6 g (0.085 mole) of methyl vinyl ketone was passed through the catalyst tube (NH$_3$ input rate 30 liter/hr). We obtained 25.2 g of catalyzate, from which 4.0 g of bases was isolated by the usual method. Distillation of 13.5 g of the bases from a Favorskii flask yields 7.2 g of 2-methyl-6-tert-butylpyridine with b.p. 170-180° (730 mm); picrate, m.p. 157-158°; a mixed melting point with the picrate of 2-methyl-6-tert-butylpyridine obtained from pinacolin and vinylacetylene was not depressed.

Catalytic treatment of acetophenone, p-methylacetophenone, and p-ethylacetophenone with methyl vinyl ketone and ammonia. Passing a mixture of 0.39 mole of the aromatic ketone and 0.13 mole of methyl vinyl ketone in a stream of ammonia over the catalyst under the conditions given above yielded catalyzates from which we isolated the bases. The bases were distilled from a Favorskii flask. In this way, from acetophenone and methyl vinyl ketone we obtained a yield of 41.2% (on methyl vinyl ketone) of 2-methyl-6-phenylpyridine with b.p. 129-130° (6 mm); picrate, m.p. 141-142°. From p-methylacetophenone [b.p. 222° (730 mm); n$_D^{20}$ 1.5243] we obtained a 31.2% yield of 2-methyl-6-(p-methylphenyl)pyridine with b.p. 139-140° (3 mm), m.p. 22°; picrate, m.p. 151°. From p-ethylacetophenone [b.p. 110° (4 mm); n$_D^{16}$ 1.5270] we obtained a 35.4% yeild (on methyl vinyl ketone) of 2-methyl--6-(p-methylphenyl)-pyridine with b.p. 145-146° (2 mm); picrate, m.p. 146-147°. The picrates of the pyridine bases obtained did not depress the melting points of picrates of individual samples obtained from the same aromatic ketones and vinylacetylene with ammonia.

SUMMARY

1. A mechanism is proposed for the catalytic condensation of vinylethynylcarbinols with ammonia.

2. A series of pyridine bases were obtained by catalytic treatment of both aliphatic and aromatic methyl ketones with methyl vinyl ketone over the catalyst Cd$_3$(PO$_4$)$_2$/Al$_2$O$_3$ at 400°.

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SYNTHESIS AND STEREOCHEMISTRY OF CORTICOSTEROID ANALOGS

COMMUNICATION 10. SYNTHESIS AND CONVERSIONS OF 3-KETO-7-METHOXY-1,2,3,9,10,10a-
HEXAHYDROPHENANTHRENE

A. A. Akhrem and I. G. Zavel'skaya

As a development of our previous investigations on the synthesis of simple analogs of corticosteroids containing the oxidized side chain characteristic of hormones of the adrenal cortex [1], it seemed interesting to study the effect of an aromatic ring in the starting ketone on the nature of nucleophilic addition at the carbonyl group and also to prepare bicyclic and tricyclic analogs of corticosteroids containing one aromatic ring.* As the starting ketone for this purpose we decided to use 6-methoxy-1-tetralone (I), which is readily synthesized from β -naphthol by a known procedure [4]. By applying the Michael reaction to ketone (I), we obtained a high yield of the tricyclic methoxy ketone 3-keto-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (III), which is an important intermediate product in the synthesis of steroid analogs. The action of ethyl formate on 6-methoxytetralone (I) in the presence of sodium methylate gave an almost quantitative yield of 6-methoxy-2-hydroxymethylene-1-tetralone (II) and condensation of the latter with methyl vinyl ketone in the presence of triethylamine in accordance with the Michael reaction gave a high yield of the crystalline ketone (III).
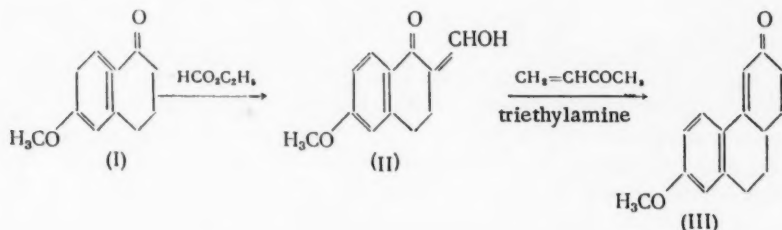
The ketone (III) was obtained previously in lower yield by a different, more complex method [5,6]. The ketone (III) was treated with vinylmagnesium bromide in tetrahydrofuran by Normant's method [7] to give an 81.0% yield of crystalline 3-vinyl-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrenol-3 (IV), oxidation of which by peracetic acid by Prilezhaev's method gave a low yield of 3-vinyl-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrenol-3-dioxide (V) of undetermined configuration.

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* Tetracyclic analogs of corticosteroids containing an aromatic ring A have recently become the subject of intensive study due to their possible use for the synthesis of 19-norcorticosteroids and also for investigating their biological activity [2]. There are also reports that some bi- and tricyclic aromatic compounds containing an α-ketol side chain have appreciable corticoid activity [3].
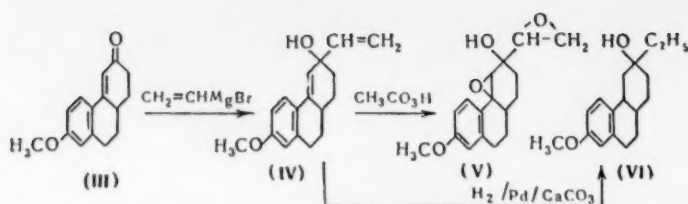
Catalytic hydrogenation of the vinyl alcohol (IV) in the presence of palladium on calcium carbonate gave liquid 3-ethyl-7-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrenol-3 (V), which was characterized as the 3,5-dinitrobenzoate with m.p. 127-128.5°. We also studied some other conversions of the tricyclic ketone (III). Thus, the action of ethyl formate on it in the presence of sodium methylate gave an 86.5% yield of crystalline 2-hydroxymethylene-3-keto-7-methoxy-1,3,9,10,10a-tetrahydrophenanthrene (VI).

Catalytic hydrogenation of the ketone (III) in the presence of palladium on calcium carbonate gave a good yield of 3-keto-7-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (VIII), which was isolated in the form of 2 isomers: a crystalline one with m.p. 123-125° (main product), giving a 2,4-dinitrophenylhydrazone with m.p. 193-195°, and a liquid one, which was characterized as the 2,4-dinitrophenylhydrazone with m.p. 162-164°. It is interesting to note that ketone (VIII), in contrast to its $\Delta^{4\,(4a)}$-dehydro analog, namely, the ketone (III), did not react with vinylmagnesium bromide by Normant's method.
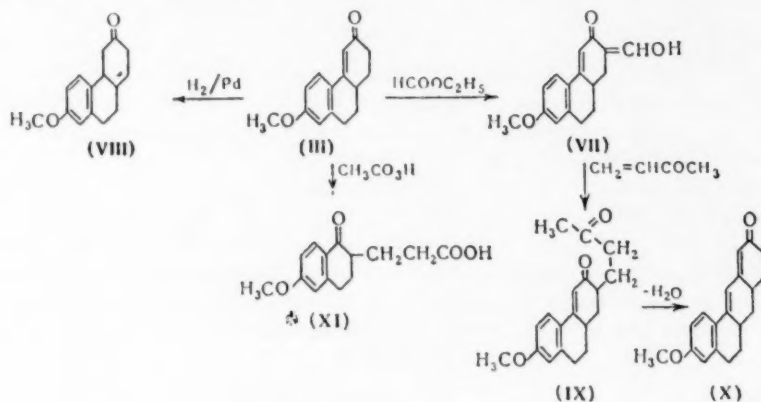
The Michael reaction with the formyl derivative of the tricyclic ketone (VII) yielded the crystalline diketone (IX). When heated with Triton B in xylene in a nitrogen atmosphere, the latter cyclized to the tetracyclic ketone (X) of the anthrasteroid series [8] with m.p. 129-131°. The presence of a carbonyl group in compound (X) was confirmed by the formation of a 2,4-dinitrophenylhydrazone and the ultraviolet spectra. The ketone (X) had strongly expresses luminescent properties.

In the oxidation of the ketone (III) with peracetic acid, there was the normal rupture of the double bond and the main reaction product was 6-methoxy-1-tetralone-2-propionic acid (XI) with m.p. 128-130°. The presence of a carbonyl group in the acid (XI) was confirmed by the formation of a 2,4-dinitrophenylhydrazone. Together with the keto acid (XI), in this experiment we isolated a small amount of a neutral product with m.p. 143-144°, which was apparently a keto oxide, though it has not been characterized in more detail as yet due to the small amount of the substance. In this connection it is interesting to note that the $\Delta^{16\,(17)}$ steroid series, the double bond in the 5-membered ring D conjugated with a C-20 carbonyl group is oxidized in 60% yield to the corresponding keto oxide both by alkaline hydrogen peroxide and by peracids [9].
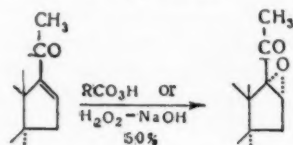
1-Vinyl-6-methoxy-1-tetralol (XII) was synthesized by the Normant reaction [7] from 6-methoxytetralone (I) and vinylmagnesium bromide. It should be mentioned that the conjugation of the tertiary hydroxyl group in the vinyl alcohol (XII) with the aromatic nucleus made it particularly labile and this apparently caused the unusual tendency of the vinyl alcohol (XII) to dehydrate under mild conditions. This may explain why the vinyl alcohol (XII) did not form an α-oxide when oxidized with peracetic acid, did not form a normal allyl isomerization product by Dimroth's method [10], and likewise was not brominated in the side chain by the action of bromine.
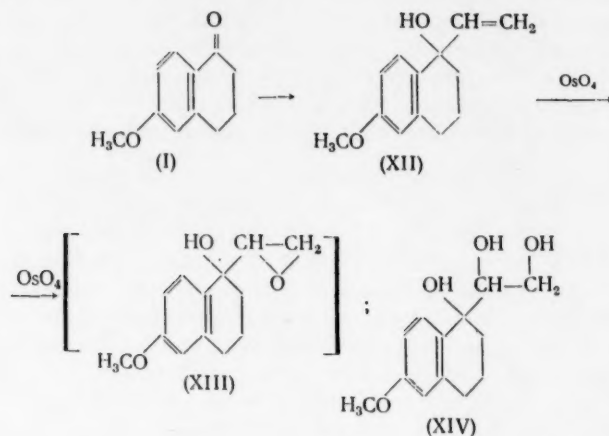
Oxidation of the vinyl alcohol (XII) with osmium tetroxide gave a low yield of a crystalline substance which corresponded in analysis to the glycidic alcohol (XIII). The normal product from the oxidation of osmic acid, namely, the triol (XIV), could not be isolated.

EXPERIMENTAL

Preparation of 6-methoxy-2-hydroxymethylene-1-tetralone (II). The sodium methylate from 10.5 g of sodium was suspended in a 150 ml of anhydrous benzene and 60 ml of ethyl formate added with stirring. The reaction mixture was stirred for a further 45 min at room temperature. A solution of 25 g of 6-methoxy-1-tetralone in 150 ml of anhydrous benzene was added over a period of an hour in a stream of nitrogen at 0-3° (bath temperature); the reaction mixture was stirred for a further 1.5 hr at room temperature. The reaction mixture was acidified with dilute sulfuric acid with cooling and the benzene layer separated, washed with water, and repeatedly extracted with 2 N potassium carbonate solution (a total of one liter). The aqueous alkaline extracts were acidified with dilute sulfuric acid and the precipitate collected, washed with water, and dried in a vacuum desiccator. We obtained 28.04 g of 6-methoxy-2-hydroxymethylene-1-tetralone (II); the yield was 97%. Recrystallization from ligroin yielded light, pale yellow crystals with m.p. 66.5-67.5°. Compound (II) gave a bright green color with an alcohol solution of ferric chloride. Found: C 70.61; 70.47; H 6.16; 6.01%. $C_{12}H_{12}O_3$. Calculated: C 70.59; H 5.90%.

Preparationof 3-keto-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (III). To a mixture of 10 g of 6-methoxy-2-hydroxymethylene-1-tetralone (II) and 6.5 g of an 80% methanol solution of methyl vinyl ketone at 0° was added 1 ml of triethylamine dropwise. The reaction mixture was kept at 0° for another hour and left at room temperature for 3 days. The reaction mixture was then dissolved in ether and washed repeatedly with an aqueous solution of sodium carbonate. The ether was distilled from the ether extract and the residue boiled in 150 ml of methanol with 6 g of KOH in 150 ml of water under nitrogen for 8 hr. The cooled reaction mixture was diluted with water and repeatedly extracted with ether (~ 1 liter). The ether extract was dried with baked sodium sulfate. Removal of the ether in vacuum and recrystallization of the crystalline residue with ethanol yielded 8.86 g of the ketone (III) as yellow platelets with m.p. 115-115.5°; the yield was 80%. Found: C 78.67; 78.74; H 6.91; 7.08%. $C_{15}H_{16}O_2$. Calculated: C 78.94; H 7.01%. $\lambda \, ^{alcohol}_{max}$ 243 and 325 mμ.

The 2,4-dinitrophenylhydrazone (DNPH) formed dark red crystals with m.p. 219-220° (alcohol–chloroform); $\lambda \, ^{alcohol}_{max}$ 408 mμ. Found: C 61.53; 61.53; H 4.90; 4.95; N 13.83; 13.91%. $C_{21}H_{20}O_5N_4$. Calculated: C 61.76; H 4.90;

N 13.72%. Literature data [5,6] for ketone: m.p. 114-115°, 115-115.5°; $\lambda_{max}^{alcohol}$ 241 and 328 mμ: for DNPH m.p. 219-220°.

Preparation of 2-hydroxymethylene-3-keto-7-methoxy-1,3,9,10,10a-pentahydrophenanthrene (VII). To the sodium methylate from 1.1 g of sodium in 25 ml of anhydrous benzene was added 6 ml of ethyl formate with stirring. After 45 min, a solution of 2.5 g of the ketone in 40 ml of benzene was added at 0-3° in a stream of nitrogen over a period of 50 min. Stirring was continued for a further 2 hr at room temperature. The cooled reaction mixture was acidified with dilute sulfuric acid and the benzene layer separated, washed with water and extracted with 2 N potassium carbonate solution (a total of 350 ml). The alkaline extract was acidified with dilute sulfuric acid; the yellow precipitate that formed was collected, washed with water, and dried in a vacuum desiccator. We obtained 2.41 g of (VII); the yield was 86.5%. Recrystallization from ethanol yielded crystals of substance (VII) with m.p. 120-122°. Compound (VII) gave a dark violet color with an alcohol solution of ferric chloride. Found: C 75.02: 75.5; H 6.31; 6.70%. $C_{16}H_{14}O_3$. Calculated: C 75.0; H 6.25%.

Oxidation of 3-keto-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (III) with peracetic acid. To 0.5 g of the ketone (III) in 10 ml of anhydrous chloroform at room temperature was added 0.6 g of 75% peracetic acid, when the temperature rose from 18 to 21°. After the reaction mixture had been kept at room temperature for 3 days, the chloroform and acetic acid were distilled from it in vacuum. The residue was extracted with ether, washed with sodium bicarbonate solution until neutral, and dried with baked magnesium sulfate. Removal of the ether from the neutral products yielded 0.08 g of a substance which melted at 143-144° after recrystallization from benzene. This substance was not investigated more closely. The aqueous alkaline solution was acidified with dilute sulfuric acid and the acid products extracted with ether. Drying the extracts with magnesium sulfate and removal of the ether yields 0.39 g of a residue, which was recrystallized from a small amount of ether. Three recrystallizations from ether yields the keto acid (XI) with m.p. 128-130°. Found: C 67.36; 67.11; H 5.08; 5.09%. $C_{14}H_{16}O_4$. Calculated: C 67.74; H 6.45%. $\lambda_{max}^{alcohol}$ 224.5 and 274 mμ.

Preparation of 3-vinyl-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrenol-3 (IV). Into a 3-necked flask fitted with a stirrer, dropping funnel, reflux condenser, thermometer, and nitrogen inlet tube were place 15 ml of anhydrous tetrahydrofuran and 1.6 g of magnesium activated with traces of iodine and then a solution of 9 g of freshly prepared vinyl bromide in 7 ml of absolute tetrahydrofuran was introduced in a nitrogen atmosphere. After the addition of ~ 1/5 of the volume of the vinyl bromide solution, a vigorous reaction began. The reaction temperature was kept at 40-45° by cooling the flask with iced water and regulating the bromide addition rate. The mixture was then boiled for 30 min, cooled to -30°, and diluted with 30 ml of anhydrous ether and then a solution of 3 g of the ketone (III) in 10 ml of tetrahydrofuran and 70 ml of anhydrous ether was added over a period of 40 min at -20 to -18°. The reaction mixture was stirred at -30 to -28° for 5 hr and left overnight. On the following day the reaction mixture was stirred and boiled gently (34-36°) under nitrogen for 2 hr, cooled, and poured into a mixture of 8 g of ammonium chloride and 50 g of ice. The ether layer was separated and the aqueous layer extracted with ether. The ether extract was dried with baked potassium carbonate. After removal of the solvent in vacuum (without heating), the residual oil (3.5 g) was extracted with ligroin (b.p. 40-50°) (a total of 300 ml). The precipitated crystals were collected. We obtained 2.73 g of product (81.0% yield).

The substance was unstable and changed during storage in a refrigerator. Three recrystallizations from ligroin yielded compound (IV) in the form of colorless crystals with m.p. 66.5-68.5°. Found: C 77.96; 77.93; H 7.69; 7.87% $(C_{17}H_{20}O_2)_3 \cdot H_2O$. Calculated: C 77.86; H 7.88%. The infrared spectrum, plotted in CCl_4 with an NaCl prism showed a band at 3640 cm^{-1} indicating the presence of a free hydroxyl group.

Preparation of 3-ethyl-7-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthren-3-ol (VI). A 0.2 g sample of the vinyl alcohol (IV) in 20 ml of ethanol was hydrogenated in the presence of palladium on calcium carbonate. After 40 min, 59 ml of hydrogen had been absorbed (theoretical amount 38 ml). The catalyst was removed by filtration and the alcohol evaporated in vacuum. This left 0.18 g of the compound (VI) as a colorless, uncrystallizable liquid. After recrystallization from ligroin, the 3,5-dinitrobenzoate of compound (VI) had m.p. 127-128.5°.

Preparation of 3-keto-7-methoxy-1,2,3,4,4a,10,10a-octahydrophenanthrene (VIII). A 1-g sample of the ketone (III) in 70 ml of methanol was hydrogenated in the presence of palladium on calcium carbonate. After 95 min, 154 ml of hydrogen had been absorbed (theoretical amount 107 ml). The catalyst was removed in vacuum and the residue (1.02 g) recrystallized from a mixture of benzene and ligroin. We isolated 0.6 g of substance (VIII) in the form of colorless crystals with m.p. 123-125° (from benzene). The infrared spectrum showed a band at

1717 cm^{-1}, indicating an unconjugated ketone. The 2,4-dinitrophenylhydrazone formed orange crystals with m.p. 193-195° (alcohol−chloroform). Chromatography of the liquid reaction products on alumina (elution with benzene−ligroin) yielded 0.3 g of a pale colored oily product, which gave a 2,4-dinitrophenylhydrazone with m.p. 162-164°; $\lambda_{max}^{alcohol}$ 364 mµ (saturated ketone).

Oxidation of the vinyl alcohol (IV) with peracetic acid. To 0.5 g of the alcohol (IV) in 50 ml of chloroform was added 0.5 g of 65% peracetic acid. The temperature rose from 18 to 21°. After being kept for six days in a refrigerator, the reaction mixture was diluted with water, the acetic acid neutralized with sodium bicarbonate, the chloroform layer separated, the aqueous layer extracted with ether, and the ether-chloroform extract dried with magnesium sulfate. Removal of the solvents and chromatography of the liquid residue (0.44 g) on alumina yielded 50 mg of the dioxide (V) in the form of colorless crystals with m.p. 120-121° (ligroin−ether). Found: C 70.61; H 7.12%. $C_{17}H_{20}O_4$. Calculated: C 70.83; H 6.94%.

Synthesis of diketone (IX). To 1 g of the formyl derivative (VII) at 0° were added 2 ml of methyl vinyl ketone and 5 drops of triethylamine. The reaction mixture gradually formed a solution. Crystallization was observed on the following day. We obtained 0.7 g of the diketone (IX) in the form of yellow crystals with m.p. 99.5-100°(ether). Found: C 76.54; 76.38; H 7.66; 7.54%. $C_{19}H_{22}O_3$. Calculated: C 76.51; H 7.38% $\lambda_{max}^{alcohol}$ 244.5 and 331 mµ. The bisdinitrophenylhydrazone melted at 206-207°.

Synthesis of tetracyclic ketone (X). A mixture of 0.2 g of trimethylbenzylammonium hydroxide and 0.64 g of the diketone (IX) in 8 ml of o-xylene was heated under nitrogen at 142° with a water trap for 4.5 hr. The cooled reaction mixture was diluted with water, extracted with ether, washed with 5% potassium hydroxide solution and water, and dried with magnesium sulfate. After removal of the solvent, the residue crystallized when ethyl acetate was added. Recrystallization yielded 0.3 g of the ketone (X) in the form of yellow crystals with m.p. 129-131°; $\lambda_{max}^{alcohol}$ 258.5 and 366 mµ (α, β-unsaturated ketone). Found: C 81.70; 81.50; H 7.68; 7.61%. $C_{19}H_{20}O_2$. Calculated: C 81.43; H 7.15%. The 2,4-dinitrophenylhydrazone formed light, dark claret colored crystals with m.p. 240-241°.

Preparation of 1-vinyl-6-methoxy-1-tetralol (XII) [7]. The conditions were the same as for the synthesis of compound (IV). From 6 g of magnesium, 35 g of vinyl bromide, and 12 g of 6-methoxy-1-tetralone we obtained 14 g of a yellow oil with $n_D^{19.5}$ 1.5500, which was the vinyl alcohol (XII). Chromatography on alumina with elution by ether yielded 11 g of the alcohol (XII) with n_D^{19} 1.5630 [7].

Oxidation of vinylmethoxytetralol (XII) with osmium tetroxide. To 0.8 g of the vinylmethoxytetralol (XII) (n_D^{20} 1.5635), in 150 ml of anhydrous ether was added 1 g of osmium tetroxide in anhydrous ether. After the reaction mixture had been kept at room temperature for 3 days, the ether was distilled from it in vacuum; the residue was boiled for 2 hr with a mixture of 10 g of sodium sulfite ($Na_2SO_3 \cdot 7H_2O$), 30 ml of water, and 30 ml of ethanol. The cooled reaction mixture was filtered, the precipitate washed with alcohol, the filtrate evaporated to dryness in vacuum, and the residue extracted for 6 hr by heating first with ether and then with ethyl acetate. Drying the extract with magnesium sulfate and removing the solvent yielded 0.4 g of a residue, consisting of an oil and crystals. The crystalline part was separated to yield 0.1 g of compound (XII) in the form of colorless crystals with m.p. 149-150.5° (ethyl acetate); Found: C 70.99; 70.90; H 7.77; 7.73%. $C_{13}H_{16}O_3$. Calculated: C 70.90; H 7.30%.

SUMMARY

1. Using the Michael reaction, from 6-methoxy-1-tetralone we synthesized the tricyclic ketone (III) in high yield and studied some of its conversions.

2. From the ketone (III) we obtained the tetracyclic ketone (X), which is a representative of a new class of compound, the so-called anthrasteroids.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation*. A complete list of the cover-to-cover English translations appears at the back of this issue.

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INFRARED SPECTRA OF CYCLOHEXANE-1,3-DIONE DERIVATIVES IN THE REGION OF 1750-1550 cm^{-1}

S. N. Ananchenko, I. V. Berezin, and I. V. Torgov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR and M. V.
Lomonosov Moscow State University

The spectra of β -diketones in the region of carbonyl group absorption are of considerable interest as they make it possible to solve the problem of the enolization of these compounds and the presence of hydrogen bonds in the enol form and also to determine the structure of polycyclic systems containing a cyclohexane-1,3-dione ring more accurately. We studied the infrared spectra of a series of cyclohexane-1,3-dione derivatives and determined the characteristics of both the diketone itself and its 2-mono- and 2,2-disubstituted derivatives. The spectra of 2,2-disubstituted derivatives of cyclohexane-1,3-dione, which are incapable of keto-enol tautomerism, were simple, as is shown by the spectrum of 2,2-dimethylcyclohexane-1,3-dione given in Fig. 1.

The spectrum consisted of two bands, of which the long-wave one was approximately 2.5 times as intense as the short-wave band. In this case it is apparently impossible to assign either of the observed bands to any particular carbonyl group. It is most probable that here there is a case of splitting of the frequency of the characteristic vibrations due to their dispersion interaction.
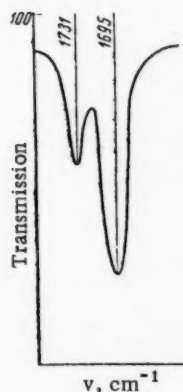
Fig. 1.

In the spectra of disubstituted cyclohexane-1,3-diones, the vibrations of the carbonyl groups appeared very characteristically. The replacement of one or both of the methyl groups by radicals which did not produce additional conjugation with the CO group, did not change the nature of the spectrum at all and, as Table 1 shows, hardly affected the position of the bands.
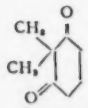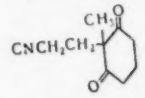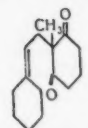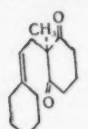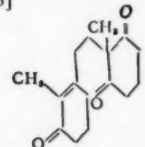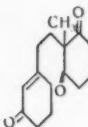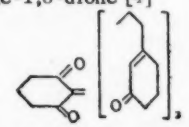
In the spectra of unsubstituted cyclohexanediones, the bands of the β -diketone grouping retained their previous form, though their frequencies were somewhat displaced toward short-wave lengths. Figure 2 shows the spectra of cyclohexane-1,3-dione and dimedone. The broad band at 1630-1631 cm^{-1} in the spectrum of cyclohexane-1,3-dione belongs to the enol form. The band of the enol form of dimedone is narrower and has ν = 1607 cm^{-1}, which agrees with the data of Rasmussen [5], who ascribed this band to the formation of hydrogen bonds on dimerization.
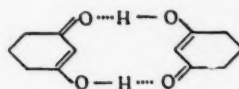
As a comparison of the two spectra presented shows, in chloroform cyclohexane-1,3-dione is enolized much more strongly than dimedone.

A characteristic of the spectra of 2-monosubstituted cyclohexane-1,3-diones is the appearance of exceptionally strong bands corresponding to the enolized forms.

TABLE 1

Compound	Frequency of bands, cm^{-1}		
	β-dicarbonyl grouping		conjugated carbonyl
	short-wave	long-wave component	
2,2-Dimethylcyclohexane-1,3-dione [1]	1731	1695	—
2-Methyl-2-(β-cyanoethyl)cyclohexane-1,3-dione [2]	1731	1697	—
2-Methyl-2-[(2'-methyl-Δ^2-cyclohexenylidene)ethyl] cyclohexane-1,3-dione [3]	1728	1696	—
2-Methyl-2-(β-cyclohexylideneethyl)cyclohexane-1,3-dione [3]	1729	1698	—
2-Methyl-2-[β-(2'-methyl-3'-keto-Δ^1-cyclohexenyl)ethyl] cyclohexane-1,3-dione [4]	1731	1701	1671
2-Methyl-2-[β-(3'-keto-Δ^1-cyclohexenyl)ethyl cyclo-hexane-1,3-dione [4]	1725	1694	1660
2,2-Di[β-(2'-methyl-3'-keto-Δ^1-cyclohexenyl)ethyl] cyclohexane-1,3-dione [4]	1728	1697	1654
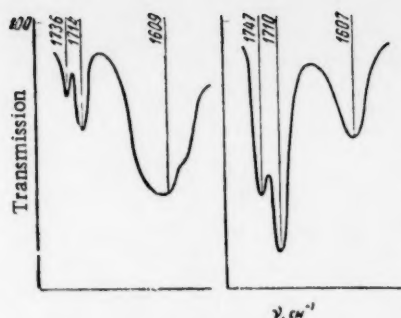
Fig. 2.
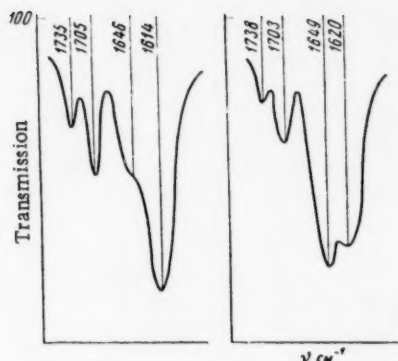
Fig. 3.

In all cases, bands of the β-dicarbonyl grouping kept the form characteristic of disubstituted cyclohexane-1,3-diones, but they were somewhat displaced toward short-wave lengths and had a low intensity in all cases. The absorption band of the enolized form lay in the region of $1614-1620$ cm^{-1} and had practically the same nature for all the compounds studied. Figure 3 gives the absorption spectra of 2-(3'-7'-dimethyl-$\Delta^{2,6}$-octadienyl)-cyclohexane-1,3-dione and 2-[β-(2'-methyl-3'-keto-Δ'-cyclohexenyl) ethyl]-cyclohexane-1,3-dione. The spectrum of the latter compound showed the band of a conjugated carbonyl group at $\gamma = 1649$ cm^{-1}. The spectra of the other compounds were the same in character as that of the former. The main frequencies are given in Table 2.

In all cases, on the short-wave side of the band at $1614-1620$ cm^{-1} there appeared a weak, difficultly resolvable band at $\nu = 1646$ cm^{-1} (at 1631 cm^{-1} in the case of 2-allylcyclohexane-1,3-dione). If following Rasmussen [5], we consider that the band at $1614-1620$ cm^{-1} corresponds to vibrations of the carbonyl in the enol dimer formed through hydrogen bonds, than this weak band may be ascribed to conjugated carbonyl in the monomeric form of the enol.

The spectrum of methylenebiscyclohexane-1,3-dione [10] has interesting characteristics, which consist of a single intense band with $\nu = 1601$ cm^{-1}. In this case there is apparently the formation of two strong intramolecular hydrogen bonds.

The character of the spectrum of 2-bromocyclohexane-1,3-dione was the same as for the monosubstituted cyclohexane-1,3-diones examined. There appeared bands of the keto and enol forms with the only difference that they all were displaced strongly toward the long-wave region. This effect of the bromine atom is unexpected as α-substituted bromo ketones have a frequency which is approximately 20 cm^{-1} greater than that of unsubstituted ketones [11]. For comparison, we also plotted the spectrum of the enol acetate of 2-methylcyclohexane-1,3-dione. As was to be expected it had only two bands: one belonging to the ester group with a frequency of 1763 cm^{-1} and a conjugated carbonyl band with the frequency of 1659 cm^{-1}.

EXPERIMENTAL
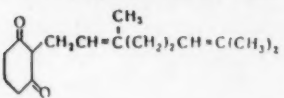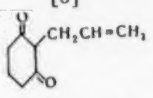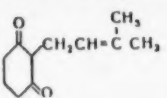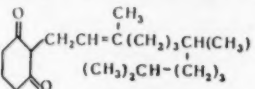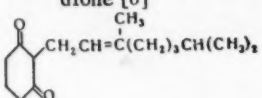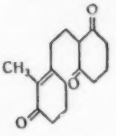
The spectra were plotted on an IKS-11 instrument with a rock salt prism. The concentration of the chloroform solutions of the substances was on an average 0.04 M with a cell thickness of 0.32 mm. The band frequencies were determined with an accuracy of ± 3 cm^{-1}.

The cyclohexane-1,3-dione had m.p. 104° and was obtained by hydrogenation of resorcinol. By alkylation of cyclohexane-1,3-dione we obtained: 2-methylcyclohexane-1,3-dione with m.p. 211-212°; 2-allylcyclohexane-1,3-dione with m.p. 124-125° [7]; 2,2-dimethylcyclohexane-1,3-dione with m.p. 39-40° [1]; 2-(γ,γ-dimethyl-allyl)cyclohexane-1,3-dione with m.p. 139-140° [8]; 2-(3',7'-dimethyl-$\Delta^{2,6}$-octadienyl)cyclohexane-1,3-dione with m.p. 101-104° [6]; 2-(3',7',11'-trimethyl-Δ^2-dodecenyl)cyclohexane-1,3-dione with m.p. 74-76° [6]; 2-(3', 7'-dimethyl-Δ^2-octenyl)cyclohexane-1,3-dione with m.p. 91-104° [6]; 2-[β-(2'-methyl-3'-keto-Δ^1-cyclohexenyl) ethyl]cyclohexane-1,3-dione with m.p. 173-175° [4]; 2,2-di-[β-(2'-methyl-3'-keto-Δ^1-cyclohexenyl)ethyl]cyclohexane-1,3-dione with m.p. 149-150° [4].

Bromination of cyclohexane-1,3-dione yielded 2-bromocyclohexane-1,3-dione with m.p. 169-170° [9]. The reaction of cyclohexane-1,3-dione with formaldehyde yielded methylenebiscyclohexane-1,3-dione with m.p. 169-170° [10]. By alkylation of 2-methylcyclohexane-1,3-dione we obtained: 2-methyl-2-[β-(2'methyl-Δ^2-cyclohexenylidene)ethyl]cyclohexane-1,3-dione with m.p. 96.5-97° [3]; 2-methyl-2-(β-cyclohexylideneethyl)cyclohexane-1,3-dione with m.p. 98-99° [3]; 2-methyl-2-[β-(2'-methyl-3'-keto-Δ^1cyclohexenyl)ethyl]cyclohexane-1,3-dione with m.p. 57-58° [4]; 2-methyl-2-[β-(3'-keto-Δ^1-cyclohexenyl)ethyl]-cyclohexane-1,3-dione with m.p. 59-60° [4]. By cyanoethylation of 2-methyl-cyclohexane-1,3-dione we obtained 2-methyl-2-β-cyanoethylcyclohexane-1,3-dione with m.p. 39-40° [2].

TABLE 2

Compound and formula	Frequency, cm^{-1}			
	β-dicarbonyl grouping		enol form, ν	conjugated carbonyl, ν
	short-wave component	long-wave component		
2-Methylcyclohexane-1,3-dione	1739	1705	1630	—
2-(3',7'-Dimethyl-$\Delta^{2,6}$-octadienyl)-cyclohexane-1,3-dione [6]	1735	1705	1614	—
2-Allylcyclohexane-1,3-dione [7]	1738	1706	1616	—
2-(γ,γ-Dimethylallyl)cyclohexane-1,3-dione [8]	1734	1705	1616	—
2-(3',7',11'-Trimethyl-Δ^2-dodecylenyl)-cyclohexane-1,3-dione [6]	1734	1706	1614	—
2-(3',7'-Dimethyl-Δ^2-octenyl)cyclohexane-1,3-dione [6]	1734	1707	1620	—
2-[β-(2-Methyl-3'-keto-Δ'-cyclohexenyl)ethyl]-cyclohexane-1,3-dione [4]	1738	1703	1620	1649
2-Bromocyclohexane-1,3-dione [8]	1672	1654	1596	—

Some of the samples were kindly provided by S. I. Zav'yalov and V. I. Gunar, to whom we are very grateful.

SUMMARY

1. In the spectra of cyclohexane-1,3-dione derivatives the β-diketone grouping produces two bands of different intensities, whose form and relative position changes little when the substutuents are replaced. A less intense band lies within the range of 1725-1739 cm^{-1} and a more intense band in the range of 1694-1707 cm^{-1}.

2. Unsubstituted and monosubstituted derivatives of cyclohexane-1,3-dione are strongly enolized in carbon tetrachloride. The enol form of monosubstituted derivatives exists as a monomer and a dimer. The bands of the enol dimer forms are quite characteristic and lie within the region of 1607-1630 cm^{-1}. The monomeric form of the enol gives a conjugated carbonyl band at a frequency of 1646-1649 cm^{-1}.

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CONDENSATION OF 2-METHYL-3-VINYL-Δ^2-CYCLOHEXENONE AND 3-VINYL-Δ^2-CYCLOHEXENONE WITH DIHYDRORESORCINOL AND METHYLDIHYDRORESORCINOL AND CYCLIZATION OF THE TRIKETONES FORMED TO HYDROPHENANTHRENE DERIVATIVES

S. N. Ananchenko and I. V. Torgov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

In a previous communication [1] we described the synthesis of 3-vinyl-Δ^2-cyclohexenone (I) and 2-methyl-3-vinyl-Δ^2-cyclohexenone (II) by condensation of enol ethers of dihydrcresorcinol and methyldihydroresorcinol with vinylmagnesium bromide.
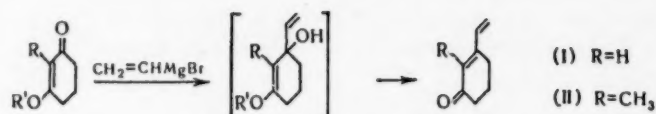
We subsequently established that instead of the ether of methyldihydroresorcinol (2-methyl-3-isobutoxy-Δ^2-cyclohexenone) it is possible to use the more accessible enol acetate (2-methyl-3-acetoxy-Δ^2-cyclohexenone) and the yield of the dienone (II) (calculated on methyldihydroresorcinol) is practically the same in both cases, though the reaction time is considerably reduced. The dienones (I) and (II) obtained are vinylogs of methyl vinyl ketone and like the latter, should readily undergo the Michael reaction with β-dicarbonyl compounds, which has previously been studied in detail in our laboratory [2]. Therefore, it seemed interesting to study the condensation of these two comparatively accessible dienones with methyldihydroresorcinol and dihydroresorcinol as this should lead to tricyclic compounds with an arrangement of functional groups suitable for building on an additional ring to yield steriod systems with angular methyl groups [in the case of the dienone (II) or methyldihydroresorcinol] or without angular methyl groups [in the case of the dienone (I) and dihydroresorcinol].

In the condensation of the dienone (II) with methyldihydroresorcinol in the presence of various alkaline agents, the primary product in all cases was 2-methyl-2-[β-(2'-methyl-3'-keto-Δ^1-cyclohexenyl)ethyl]cyclohexane-1,3-dione (III). The best yield (70%) was obtained with trimethylbenzylammonium hydroxide (Triton B). In the presence of piperidine phosphate, the yield of the triketone (III) was 45%, in the presence of pyridine or potassium tert-butylate, 25%, and in the presence of triethylamine, 20%.

(II)   (III)
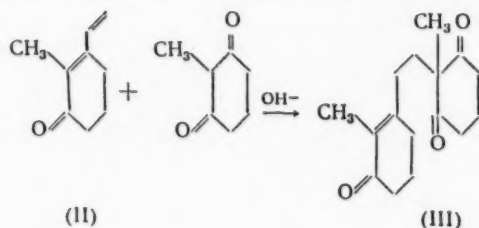
The structure of the triketone (III) was established by the ultraviolet spectrum, which showed a maximum with λ_{max} 246 mµ (lg ε 4.21), that is characteristic of α,β-unsaturated ketones, and also by the infrared spectrum which showed the frequencies of 1731 and 1701 cm^{-1}, that are typical of disubstituted dihydroresorcinols [3]. When heated with a solution of p-toluenesulfonic acid in a mixture of acetic acid and toluene, the triketone (III) formed 8,11-dimethyl-$\Delta^{8(14),12}$-decahydrophenanthrene-1,7-dione (IV). In one of the experiments, as a by-product we isolated 8,11-dimethyl-$\Delta^{8(14)}$-dodecahydro-12-phenanthrol-1,7-dione (V), which is an intermediate product in the formation of the diketone (IV).
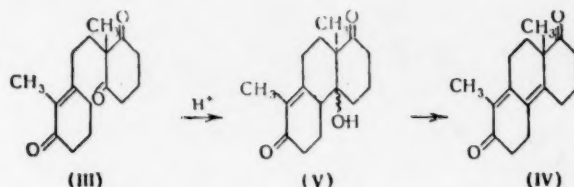
The ketol (V) and the dione (IV) were obtained previously by Eschenmoser and his coworkers [4] by a somewhat different rout through 2-methyl-3-ethynyl-Δ^2-cyclohexenone; their constants and also the spectral data agreed completely with the data of the Swiss chemists.

Condensation of the dienone (II) with dihydroresorcinol in the presence of potassium tert-butylate formed a mixture of mono- and disubstituted dihydroresorcinols: 2-[β-(2'-methyl-3'-keto-Δ^1-cyclohexenyl)ethyl]cyclohexane-1,3-dione (VI) in 65% yield and 2,2-di-[β-(2'-methyl-3'-keto-Δ^1-cyclohexenyl)ethyl]-cyclohexane-1,3-dione (VII) in 18% yield. When potassium hydroxide in aqueous dioxane was used as the condensing agent, we isolated 23% of the trione (VI) and 25% of the tetraone (VII).
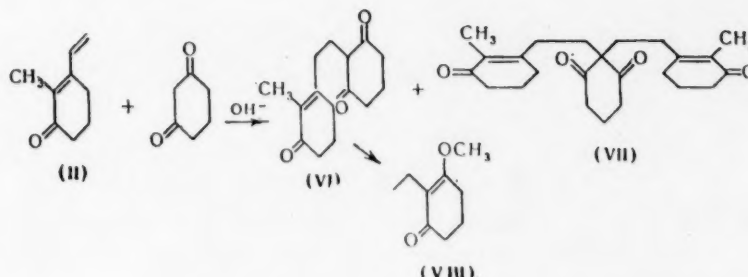
The use of Triton B or piperidine phosphate did not give positive results. The structure of the ketones (VI) and (VII) was established by the ultraviolet and infrared spectra and was confirmed by the reactions of the triketone (VI) which dissolved in alkalis and readily gave the methyl ether (VIII) with diazomethane, analogously to methyldihydroresorcinol. In contrast to the case of the triketone (III), all attempts to cyclize the diketone (VIII) and the tetraketone (VII) were unsuccessful.

Condensation of the dienone (I) with methyldihydroresorcinol gave the best results in the presence of potassium hydroxide, when 2-methyl-2-[β-(3'-keto-Δ^1-cyclohexenyl)ethyl]cyclohexane-1,3-dione (IX) was formed in 45% yield. The use of piperidine phosphate led to the cyclization product 11-methyl-$\Delta^{8(14),12}$-decahydro-phenanthrene-1,7-dione (X) and when the reaction was carried out in the presence of potassium tert-butylate, it was possible to isolate from the reaction mixture only a 5% yield of the tricyclic ketol 11-methyl-$\Delta^{8(14)}$-dodeca-hydro-12-phenanthrol-1,7-dione (XI) (see scheme on next page).

The structures of compounds (X) and (XI) were assigned on the basis of the similarity of their ultraviolet and infrared spectra to those of the compounds (IV) and (V) respectively. Thus, for (X) we found λ_{max} 307 mµ (lg ε 4.22) and the frequencies of 1715 and 1665 cm^{-1}, while for the diketone (IV), λ_{max} 313 mµ (lg ε 4.22) 1708 and 1650 cm^{-1}. For the ketol (XI) we found the frequencies 1709 and 1672 cm^{-1} as compared with 1703 and 1663 cm^{-1} for the ketol (V).

CH₃ ... (X) ... $C_5H_{11}N$ / H_3PO_4 ... + ... (I) ... KOH ... CH₃ ... (IX)

t-C₄H₉OK ... $C_7H_9SO_3H$

(XI) ... (XII)
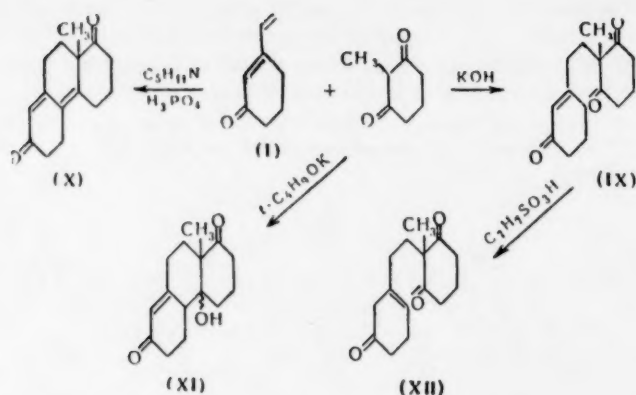
In an attempt at the cyclization of the triketone (IX) under the same conditions as for the triketone (III), we isolated only the isomeric triketone (XII). Since its infrared spectrum had the frequencies 1739 cm^{-1} and 1708 cm^{-1}, which are close to the frequency of disubstituted dihydroresorcinols (1731 cm^{-1}), and the ultraviolet spectrum had λ_{max} 292 mμ (lg ε 2.04), which is characteristic of allyl ketones, we assigned to it the above structures.

In the condensation of the dienone (I) with dihydroresorcinol in the presence of potassium hydroxide, i.e., under conditions analogous to the preparation of the triketone (VI), we isolated a ketone with the formula $C_{14}H_{18}O_3$, which was insoluble in alkalis, was not dehydrated by heating with p-toluenesulfonic acid in benzene, and did not contain active hydrogen according to a Tserevitinov test. On the basis of these facts we consider that of the two possible formulas (XIII) and (XIV), the latter is more probably as the β-ketol (XIII) should readily lose the elements of water like the ketol (V), for example.

(I) + ... OH^- ... (XIV) ... (XIII)
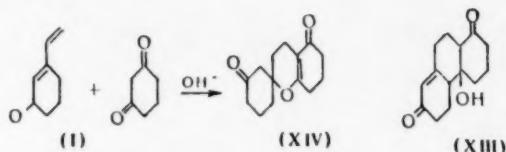
We have reported previously that bicyclic enol ethers of dihydroresorcinol are formed readily [5]. Thus, when heated with phosphorus pentoxide, 2-(γ,γ-dimethylallyl)-cyclohexane-1,3-dione gave 2,2-dimethyltetrahydro-5-chromanone instead of the expected bicyclic ketone.

Of all the tricyclic compounds described above, the most interesting for subsequent conversion to steroids are the diketones (IV) and (X). We made a series of attempts to build up ring A by condensing the diketone (IV) with methyl vinyl ketone under various conditions, but they were unsuccessful.

In the reduction of the diketone (IV) with NaBH₄, only the unconjugated CO group was reduced selectively with the formation of 8,11-dimethyl-$\Delta^{8(14),12}$-decahydro-1-β-phenanthrenol-7-one (XV), which gave the acetate (XVa).

(IV) ... NaBH₄ ... (XV) ... Ac₂O ... (XVa) ... (XVI)
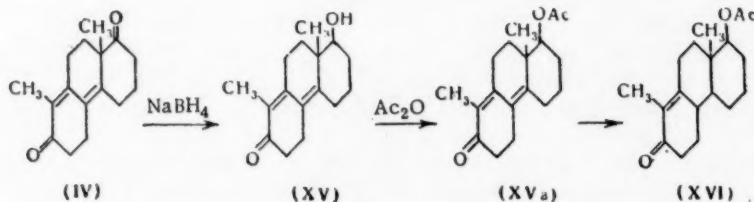
For the preparation of the acetate (XVa) it was possible to use the unpurified cyclization product of the triketone (III) and then the over-all yield reached 70%.

The structure of the ketol (XV) was assigned on the basis of the ultraviolet spectrum. The configuration of the hydroxyl was adopted in analogy with literature data [6]. In the hydrogenation of the acetate (XVa) we isolated a small amount of a crystalline product, which, judging by its ultraviolet spectrum, was the acetate of 8,11-dimethyl-$\Delta^{8(14)}$-dodecahydro-1β-phenanthrenol-7-one (XVI). No attempt to condense the ketol (XV) or its acetate (XVa) with methyl vinyl ketone or isopropenyl methyl ketone by the Mannich-Robinson or Michael methods led to the desired results.

<center>EXPERIMENTAL</center>

Preparation of 2-methyl-3-vinyl-Δ^2-cyclohexenone (II). a) From 2-methyl-3-isobutyoxy-Δ^2-cyclohexenone [b.p. 103-105° (0.5 mm); n_D^{20}, 5015]. To a solution of vinylmagnesium bromide (from 7 g of magnesium, 31 g of freshly prepared vinyl bromide, and 170 ml of tetrahydrofuran) was added a solution of 20 g of 2-methyl-3-isobutoxy-Δ^2-cyclohexenone [4] in 20 ml of ether with stirring at a temperature no higher than -15°. The mixture was left on ice overnight and on the following day, heated at 50-60° for 30 min and decomposed at 0° with ice and dilute hydrochloric acid. The product was extracted with ether and the extract washed successively with sodium thiosulfate solution, sodium carbonate solution, and water, and dried with magnesium sulfate. Distillation yielded 10.7 g (65%) of 2-methyl-3-vinyl-Δ^2-cyclohexenone (II) with b.p. 67-68.5° (2 mm); n_D^{20} 1.5512; d_4^{20} 0.996 [1].

b) From 2-methyl-3-acetoxy-Δ^2-cyclohexenone [5] [b.p. 106-108° (5 mm); n_D^{20} 1.4860]. The reaction was carried out as above (with 2 moles of magnesium to 1 mole of enol acetate), but at -50 to -60°. The yield of the dienone (II) was 60%. The dienone did not react with maleic anhydride or quinone either at 20° or on boiling in benzene.

Preparation of 3-ethoxy-Δ^2-cyclohexenone. A mixture of 150 g of dihydroresorcinol, 300 ml of alcohol, 1200 ml of benzene, and 1 g of p-toluenesulfonic acid was boiled with stirring in a flask with a reflux condenser fitted with a water trap until the separation of water ceased (this required 26 hr and 22 ml of water was collected as compared with 24 ml according to theory). The mixture of benzene and alcohol was removed in vacuum and the residue treated with sodium carbonate solution, washed with water, and dried with magnesium sulfate. Distillation yielded 156 g (84%) of 3-ethoxy-Δ^2-cyclohexenone with b.p. 85-86° (1.5 mm); n_D^{20} 1.5050.

Preparation of 3-vinyl-Δ^2-cyclohexenone (I). To a solution of vinylmagnesium bromide (from 16 g of magnesium, 100 g of vinyl bromide, and 200 ml of absolute ether and then a solution of 47 g of 3-ethoxy-Δ^2-cyclohexenone in 50 ml of absolute ether was gradually added at such a rate that the temperature was kept below -15°. The reaction mixture was left on ice overnight and heated for 1 hr at 40° on the following day. The treatment described for the dienone (II) and distillation yielded 30 g (75%) of 3-vinyl-Δ^2-cyclohexenone (I) with b.p. 82-83° (4 mm) and n_D^{20} 1.5488 [1]. The dinitrophenylhydrazone had m.p. 169-170° (from alcohol-dioxane); λ_{max} (in alcohol) 377 mμ. Found: N 18.9; 19.0%. $C_{14}H_{14}O_4N_4$. Calculated: N 18.5%.

Like the dienone (II), the dienone (I) did not react with maleic anhydride or quinone either at 20° or when the components were boiled in benzene.

Condensation of 2-methyl-3-vinyl-Δ^2-cyclohexenone (II) with methyldihydroresorcinol. a) With Triton B. A mixture of 17 g of the dienone (II), 17 g of methyldihydroresorcinol, Triton B (from 1 g of the hydrochloride and 3.5 ml of an 8% alcohol solution of potassium hydroxide), and 30 ml of xylene was heated in a stream of nitrogen with the condenser in the position for distillation until the alcohol and part of the xylene had distilled and then under reflux at 120° (bath temperature) for 12 hr. The reaction mixture was diluted with 100 ml of ether, washed twice with dilute hydrochloric acid and three times with sodium carbonate solution, and dried with magnesium sulfate. After removal of the ether, the residue was diluted with 5-7 ml of ether and left to crystallize at 0°. We obtained 18.2 g of the triketone (III) with m.p. 57-58°. From the mother solutions we isolated a further 2 g of product with m.p. 56-57°. The total yield was 70%; λ_{max} (in alcohol) 246 mμ (lg ε 4.21), infrared spectrum: 1731, 1701, 1671 cm^{-1}. Found: C 73.4; 73.4; H 8.5; 8.4%. $C_{16}H_{22}O_3$. Calculated: C 73.5; H 8.5%.

b) With piperidine phosphate. A mixture of 2.85 g of the dienone (II), 3 g of methyldihydroresorcinol, 4 ml of xylene, 2 ml of pyridine, and 0.4 g of piperidine phosphate (3 moles of piperidine to 1 mole of acid) was heated in a stream of nitrogen at 100° for 10 hr and at 120° for 20 hr, by which time the bulk of the methyldihydroresorcinol had dissolved. Treatment as described above yielded 2.5 g (45%) of the triketone (III) with m.p. 52—54°.

c) With pyridine. A mixture of 2.8 g of the dienone (II), 2.5 g of methyldihydroresorcinol, 3 ml of pyridine and 2 m l of xylene was heated in a stream of nitrogen at 130-135° for 90 hr. The normal treatment yielded 1.4 g (25%) of the triketone (III) with m.p. 55-56°.

d) With triethylamine. A mixture of 7 g of the dienone (III), 7 g of methyldihydroresorcinol, 10 ml of tri-ethylamine, 30 ml of benzene, and 20 ml of toluene was boiled in a flask with a reflux condenser fitted with a water trap for 8 hr. No separation of water was observed, though the methyldihydroresorcinol dissolved completely. The brown mixture was diluted with 50 ml of ether and washed twice with cold 20% hydrochloric acid to remove the amine and twice with 20% sodium carbonate solution. The ether solution was dried with magnesium sulfate, filtered, and evaporated in vacuum. The residue was diluted with 3 ml of ether and left to crystallize. Crystallization began only after 18 months; the yield of the triketone (III) with m.p. 55-56° was ~20%.

e) With potassium tert-butylate. A mixture of 4.3 g of the dienone (II), 4 g of methyldihydroresorcinol, a solution of potassium tert-butylate (from 0.15 g of potassium and 8 ml of tert-butanol), and 10 ml of xylene was boiled for 5 hr under reflux in a stream of nitrogen. The tert-butanol was then distilled from the mixture, which was heated at 120° for a further 25 hr (in a stream of nitrogen). The normal treatment yielded 2.1 g (25%) of the triketone (III) with m.p. 45-54°.

Cyclization of triketone (III). A solution of 5 g of the triketone (III) and 0.5 g of p-toluenesulfonic acid in 10 ml of acetic acid and 30 ml of toluene was boiled in a flask with a reflux condenser fitted with a water trap for 9 hr, by which time the separation of water had ceased. The mixture was diluted with 50 ml of ether, washed 7-8 times with water and twice with 10% sodium carbonate solution, dried with magnesium sulfate, and filtered and the solvent removed by distillation. The residue was dissolved in absolute ether and filtered twice through alumina (10 g portions). Removal of the ether and keeping the residue at 0° yielded 1.9 g (40%) of the diketone (IV) with m.p. 72-73.5°; λ_{max} (in alcohol) 246,313 mμ (lg ε 3.74 and 4.22); infrared spectrum 1708, 1605 cm^{-1}.

In one experiment of cyclization, we obtained a 10% yield of the ketol (V) with m.p. 166-170° (from ben-zene-ligroin); infrared spectrum 1703 and 1663 cm^{-1}. Eschenmoser [4] gives for the diketone (IV) m.p. 70-72°, and for the ketol (V), m.p. 171°.

Condensation of dienone (II) with dihydroresorcinol. a) With potassium tert-butylate. To a solution of alcoholate (from 0.3 g of potassium and 10 ml of tert-butanol) was added 4.1 g of dihydroresorcinol, the mixture stirred for 20 min, 5 g of the dienone (II) and 5 ml of tert-butanol were added, and the mixture was boiled for 9 hr. All operations were carried out in a stream of nitrogen. The alcohol was removed in vacuum, the residue stirred for 20 min with 25 ml of saturated sodium carbonate solution and extracted with chloroform, and the ex-tract dried with magnesium sulfate. Removal of the solvent yielded 2 g (18%) of the tetraketone (VII) with m.p. 149-150° (from ethyl acetate); λ_{max} (in alcohol) 246 mμ (lg ε 4.46); infrared spectrum 1723, 1697, 1654, 1629 cm^{-1}. Found: C 73.8; 74.0; H 8.3; 8.3%. $C_{24}H_{32}O_4$. Calculated: C 73.9; H 8.4%.

The aqueous alkaline solution was acidified with hydrochloric acid (to Congo) at 0° to yield 5.2 g (65%) of the triketone (VI) with m.p. 173-175° (from alcohol); λ_{max} (in alcohol) 255.5, 286 mμ (lg ε 4.34, 4.12). Infrared spectrum 1738, 1717 and 1650 cm^{-1}. Found: C 72.1; 72.4; H 8.5; 8.4%. $C_{15}H_{20}O_3$. Calculated: C 72.55; H 8.1%.

b) With potassium hydroxide. To a cooled solution of 0.75 g of potassium hydroxide in 8 ml of water and 14 ml of dioxane was added 9.3 g of dihydroresorcinol at 0°, the mixture stirred for 20 min, a solution of 11.2 g of the dienone (II) in 18 ml of dioxane added, and the mixture heated at 100° for 18 hr. The cooled reaction mix-ture was treated with 5 ml of water and left overnight. By next day there had precipitated 6.2 g of crystals (25%) of the tetraketone (VII) with m.p. 145-147°. By the usual method, from the mother solution we isolated 4.2 g (23%) of the triketone (VI) with m.p. 169-172°. Carrying out this reaction with a twofold excess of dihydroresorcinol gave 28% of (VI) and 22% of (VII). All attempts to cyclize the triketone (VI) with Triton B, piperidine phosphate, or potassium tert-butylate led to a mixture of uncrystallizable products, which could not be separated by chromato-graphy on alumina.

Preparation of methoxy diketone (VIII). To a solution of 5 g of the triketone (VI) in 50 ml of ether was added an ether solution of diazomethane to a permanent yellow color, the mixture left for 3 hr, and the ether re-moved. Recrystallization of the residue from benzene yielded 2.9 g of 1-methoxy-2-β(2'-methyl-1'-keto-Δ^2-cyclohexenyl)ethyl]-Δ^1-cyclohexen-3-one (VIII) with m.p. 125-126°. Found: C 73.5; 73.5; H 8.4; 8.5%. $C_{16}H_{22}O_3$. Calculated: C 73.2; H 8.45%.

Shaking the methoxy diketone (VIII) with 3% hydrochloric acid for 5 min formed the triketone (VI). All attempts to cyclize the methoxy diketone (VIII) [with potassium tert-butylate in benzene (20°, 2.5 hr), with sodium ethylate in xylene (boiling for 10 hr), with an aqueous dioxane solution of potassium hydroxide at 20° (3 hr), and with piperidine phosphate in xylene (150, 10 hr)] were unsuccessful and the ketone (VIII) was recovered in all cases.

Condensation of dienone (I) with methyldihydroresorcinol. a) With potassium hydroxide. To a solution of 0.4 g of potassium hydroxide in 3.5 ml of water and 12 ml of dioxane was added 5 g of methyldihydroresorcinol, the mixture stirred for 20 min, a solution of 5 g of the dienone(I) in 5 ml of dioxane added, and the mixture heated at 100° for 12 hr. All operations were carried out in a stream of nitrogen. The cooled mixture was treated with 2 ml of hydrochloric acid(1 : 1), stirred for 5 min, and extracted three times with chloroform. The extract was washed with sodium carbonate solution until the wash waters were colorless and then with water and dried with magnesium sulfate. Removal of the solvent in vacuum, dilution of the residue with a small amount of ether, and crystallization yielded 4.52 g(45%) of the triketone(IX) with m.p. 59-60°; λ_{max}(in alcohol) 235.5 mμ (lg ϵ 4.19). Found: C 72.6; 72.3; H 8.1; 8.1%. $C_{15}H_{20}O_3$. Calculated : C 72.55; H 8.1%.

b) With pyridine. A mixture of 4 g of the dienone (I), 3.8 g of methyldihydroresorsinol, 4.5 ml of pyridine, and 3.5 ml of xylene was heated in a stream of nitrogen at 130-140° for 96 hr. Treatment as described in the preparation of the triketone (III) yielded an oil (2.5 g), which, after standing in a refrigerator for 11 months, gave 0.12 g (1.5%) of the triketone (IX) with m.p. 54−58°. Attempts to carry out this condensation with Triton B were unsuccessful.

Isomerization of triketone (IX). a) A mixture of 4.5 g of the triketone (IX), 10 ml of glacial acetic acid, 30 ml of toluene, and 0.5 g of p-toluenesulfonic acid was boiled in a nitrogen atmosphere in a flask with a reflux condenser fitted with a water trap for 8 hr. The reaction mixture was diluted with 50 ml of ether, washed four times with water and seven times with sodium carbonate solution, dried with magnesium sulfate, and filtered through a column with 30 g of alumina. Evaporation of the filtrate yielded 1.2 g (27%) of the isomeric ketone (XII) with m.p. 107-108°; λ_{max} (in alcohol); 292 mμ (lg ε 2.04); infrared spectrum 1739 and 1708 cm^{-1}. Found: C 72.6; 72.7; H 8.0; 8.0%. $C_{15}H_{20}O_3$. Calculated: C 72.55; H 8.1%.

b) A mixture of 9.5 ml of acetic acid and 28 ml of toluene was boiled to remove traces of water, 4.2 g of the triketone (IX), 0.5 g of p-toluenesulfonic acid, and 10 mg of iodine were added, and the mixture was again boiled for 15 min. Treatment as described above yielded 1.7 g (40%) of the ketone (XII) with m.p. 107-108°.

Preparation of diketone (X). A mixture of 8 g of the dienone (I), 8 g of methyldihydroresorcinol, 6 ml of pyridine, 5 ml of xylene, 1.5 ml of piperidine, and 0.7 g of phosphoric acid was heated at 110-120° and stirred in a stream of nitrogen for 10 hr. The reaction mixture was diluted with 50 ml of ether, washed with 20% hydrochloric acid, saturated sodium carbonate solution, and water, and dried with magnesium sulfate. After removal of the solvent, the residue partly crystallized. We obtained 4 g (26%) of the diketone (X) with m.p. 67-68° (from alcohol); λ_{max} (in alcohol) 307 mμ (lg ε 4.22); infrared spectrum 1715, 1665, and 1615 cm^{-1}. Found: C 78.4; 78.1; H 8.1; 8.05%. $C_{15}H_{18}O_2$. Calculated: C 78.2; H 7.9%.

Attempts to prepare the diketone (X) by cyclization of the triketone (IX) with phosphorus pentoxide in acetic acid led only to the formation of small amounts of the isomeric ketone (XII).

Preparation of hydroxy ketone (XII). To a solution of alcoholate (from 0.3 g of potassium and 10 ml of tert-butanol) was added 4.1 g of methyldihydroresorcinol, the mixture stirred for 20 min, a solution of 4 g of the dienone (I) in 5 ml of tert-butanol added, and the mixture boiled in a stream of nitrogen for 9 hr. After the mixture had cooled, the tert-butanol was removed in vacuum and the residue stirred for 20 min with 25 ml of saturated sodium carbonate solution and extracted with chloroform. The extract was dried with magnesium sulfate, the solvent removed, and the residue recrystallized from alcohol to yield 0.30 g (5%) of the hydroxy ketone (XI) with m.p. 151-152°; λ_{max} (in alcohol) 242, 302 mμ; infrared spectrum 1709, 1672 cm^{-1} (in chloroform). Found: C 72.50; 72.65; H 8.4; 8.3%. $C_{15}H_{20}O_3$. Calculated: C 72.55; H 8.1%.

Heating the hydroxy ketone (XI) with p-toluenesulfonic acid in acetic acid formed an oil from which it was impossible to isolate the tricyclic diketone (X).

Condensation of dienone (I) with dihydroresorcinol. To a solution of 0.6 g of potassium hydroxide in 6 ml of water and 10 ml of dioxane cooled to 0° was added 7.3 g of dihydroresorcinol, the mixture stirred for 20 min at 20°, a solution of 8 g of the dienone (I) in 5 ml of dioxane added, and the mixture boiled for 15 hr. All operations were carried out in a stream of nitrogen. The reaction mixture was stirred for 10 min with 10 ml of hydrochloric acid (1:1) and extracted with chloroform. The extract was washed three times with warm water to remove dihydroresorcinol, dried with magnesium sulfate, and filtered through a column with alumina (20 g) and the solvent removed. We obtained 6.5 g (43%) of the diketone (XIV) with m.p. 79-81° (from alcohol−ether); λ_{max} 259 mμ (lg ε 4.26); infrared spectrum 1717, 1646 and 1614 cm^{-1}. The compound was insoluble in sodium carbonate and sodium hydroxide solutions and did not contain labile hydrogen according to a Tserevitinov test. Found: C 71.3; 71.4; H 7.8; 7.8%. $C_{14}H_{18}O_3$. Calculated: C 71.7; H 7.7%.

Preparation of ketone (XV). To a solution of 1 g of the diketone (IV) in 8 ml of alcohol at 20° was added a suspension of 0.15 g of sodium borohydride in 10 ml of alcohol and the mixture left for 12 min. The excess reducing agent was then decomposed by the addition of 2 ml of acetic acid, the mixture evaporated in vacuum, and the residue shaken with water and extracted with chloroform. The extract was dried with magnesium sulfate and filtered, the solvent removed, and the residue recrystallized from ether to yield 0.6 g of the ketol (XV) with m.p. 131-132°; λ_{max} (in alcohol) 310 mμ (lg ϵ 4.315); infrared spectrum 1648 cm^{-1}. Found: C 77.9; 77.7; H 9.0 9.05%. $C_{16}H_{22}O_2$. Calculated: C 78.0; H 9.0%. The 2,4-dinitrophenylhydrazone had m.p. 219-220° (from ethyl acetate—dioxane); λ_{max} (in alcohol) 404 mμ. Found: N 13.4%. $C_{22}H_{26}O_5N_4$. Calculated: N 13.1%.

Hydrogenation of the ketol over Pd/CaCO$_3$ in a mixture of alcohol and pyridine until 1 mole of hydrogen had been absorbed yielded an uncrystallizable mixture of products.

Preparation of acetate of ketol (XV). A mixture of 1.3 g of the ketol (XV) with 5 ml of acetic anhydride and 6 ml of pyridine was kept at 20° for 3 days, the solvent removed in vacuum, and the residue treated with water and extracted with ether. The extract was washed with dilute hydrochloric acid and then water, dried with magnesium sulfate, filtered and evaporated. Recrystallization of the residue from alcohol yielded 1.1 g of the acetate of the ketol (XV) with m.p. 116-117°; λ_{max} (in alcohol) 306 mμ (lg ϵ 4.318); infrared spectrum 1722, 1644 cm^{-1} (chloroform). Found: C 75.1; 75.05; H 8.5; 8.3%. $C_{18}H_{24}O_3$. Calculated: C 75.0; H 8.4%. If the unpurified diketone (IV) was reduced and the reaction product acetylated without isolation of the immediate ketol (XV), the yield of the ketol acetate reached 70%.

Hydrogenation of the acetate of the ketol (XV) over Pd/CaCO$_3$ in ethyl acetate to the absorption of 1 mole of hydrogen formed a mixture of products, from which it was possible to isolate in low yield (2%) a crystalline compound with m.p. 134-135°, which corresponded in ultraviolet spectrum to an α,β-unsaturated ketone (λ_{max} 260 mμ, lg ϵ 4.713), but corresponded in analysis only to the product of complete hydrogenation (Found: C 73.8; H 9.6%. Calculated: C 73.9; H 9.7%).

Attempts to convert tricyclic ketones to tetracyclic ketones. Attempts were made to add methyl vinyl ketone to the diketone (IV) in the presence of sodium ethylate and potassium tert-butylate and to add 3-methyl-4-di-methylamino-2-butanone iodomethylate to the diketone (IV) by the Mannich—Robinson method. In all these cases we obtained only high-molecular products. Attempts to add methyl vinyl ketone to the diketone (X) in the presence of: a) sodium ethylate and potassium tert-butylate at -15 and 20°; b) piperidine phosphate in the presence of free piperidine at 110-120°; c) diethylaniline and triethylamine at 260° (30 min) likewise did not give positive results.

In the reaction of methyl vinyl ketone with the ketol (XV) or its acetate in the presence of potassium tert-butylate, the starting tricyclic compounds were recovered. The same results were obtained in the condensation with 3-methyl-4-dimethylamino-2-butanone iodomethylate by the Mannich—Robinson method.

SUMMARY

1. Condensation of 3-vinyl-Δ^2-cyclohexenone (I) and 2-methyl-3-vinyl-Δ^2-cyclohexenone (II) with methyl-dihydroresorcinol in the presence of alkaline agents formed the bicyclic triketones (IX) and (III), respectively. Condensation of the dienone (II) with dihydroresorcinol formed the triketone (VI) of analogous structure together with the disubstituted derivative of dihydroresorcinol (VII).

2. Condensation of the dienone (I) with dihydroresorcinol, in contrast to the previous examples, yielded an addition product for which the structure (XIV) is proposed.

3. The triketone (III) was readily cyclized by acid agents to the tricyclic diketone (IV) or the corresponding ketol (V). The triketone (IX), which has a similar structure, was not cyclized under these conditions, but the corresponding diketone (X) was obtained by condensation of the dienone (I) with methyl dihydroresorcinol under the action of piperidine phosphate. The triketone (VI) could not be cyclized.

4. In the reduction of the diketone (IV) with sodium borohydride, the unconjugated CO group was reduced selectively to form the ketol (XV).

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CHEMISTRY OF ACETALS

COMMUNICATION 2. REACTION OF ACETAL WITH DIKETENE AND WITH ACETOACETIC ESTER

S. S. Yufit and V. F. Kucherov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR
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Continuing the study of the conversions of acetals [1], we decided to investigate the reactions of acetal with diketene and with acetoacetic ester for their subsequent use as a new method of lengthening carbon chains. It was found that the reaction of acetal with diketene in the presence of boron trifluoride etherate forms a mixture of products and the determination of their structures and the probable scheme for their formation is the subject of the present communication.

From the reaction products of diketene and acetal we isolated three products: 2-(1'-ethoxy)ethylacetoacetic ester (I), 1,1,3-triethoxybutane (II), and 2-(1',3'-diethoxy)butylacetoacetic ester (III).

$$
\begin{array}{l}
CH_3-C=CH \\
\quad\ \ |\qquad | \\
\quad\ \ O-C=O \\
CH_3CH(OC_2H_5)
\end{array}
\left.\vphantom{\begin{array}{c}a\\a\\a\end{array}}\right\}
\rightarrow
\begin{array}{c}
CH_3-CH-OC_2H_5 \\
\qquad\quad | \\
CH_3-C-CH-COOC_2H_5 \\
\quad\ \ \| \\
\quad\ \ O \\
(I)
\end{array}
+
\begin{array}{c}
OC_2H_5 \\
| \\
CH_3-CH-CH_2-CH(OC_2H_5)_2+ \\
(II)
\end{array}
$$

$$
+CH_3-C-CH
\begin{array}{c}
CH_3 \\
| \\
CH_2-CH-OC_2H_5 \\
| \\
CH-OC_2H_5 \\
\end{array}
$$
$$
\begin{array}{cc}
\| & \ \ \backslash \\
O & COOC_2H_5 \\
& (III)
\end{array}
$$
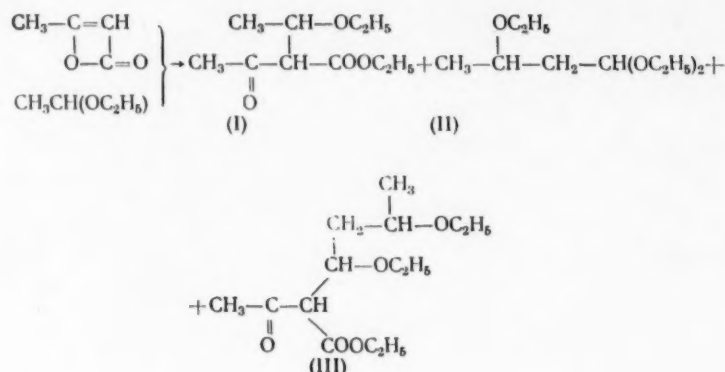
The main reaction product was 2-(1'-ethoxy)ethylacetoacetic ester (I) and this was formed in up to 50% yield as a result of direct alkylation of diketene with the formation of a new carbon—carbon bond. Its structure was established by acid hydrolysis to ethylideneacetoacetic ester (IV) and ethylideneacetone (V), which were characterized through crystalline 2,4-dinitrophenylhydrazones and spectra.

A conclusive demonstration of the structure of the ester (I) was obtained by studying the reaction of acetal with acetoacetic ester. As we showed for the first time, this reaction in the presence of such a catalyst as BF_3 etherate gives up to 70% yield of 2-(1'-ethoxy)ethylacetoacetic ester (I). This reaction evidently may be a general method of lengthening a carbon chain. (See scheme on next page).

As will be shown below, under the conditions of the reaction of diketene with acetal there is elimination of alcohol from the acetal so that 2-(1'-ethoxy) ethylacetoacetic ester (I) may be formed both by direct reaction

$$CH_3COCH_2COOC_2H_5 + CH_3CH(OC_2H_5)_2 \rightarrow CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{COOC_2H_5}{|}}{\overset{\overset{CH_3}{\overset{|}{CH-OC_2H_5}}}{C}}-H \quad \xrightarrow{HCl}$$

$$(I)$$

$$\rightarrow CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{COOC_2H_5}{\diagdown}}{\overset{\overset{CH-CH_3}{\diagup}}{C}} \qquad \rightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH=CH-CH_3$$

$$(IV) \qquad\qquad (V)$$

of acetal with diketene and by a secondary reaction of acetal with acetoacetic ester, obtained by the reaction of diketene with alcohol. It might also be considered that 2-(1'-ethoxy)ethylacetoacetic ester (I) could be formed by the reactions of acetal with 3-ethoxycrotonic ester, acetoacetic ester with vinyl ether [2], or, finally, diketene with vinyl ether. Special experiments showed that in the first two cases the reaction gives only insignificant yields while in the latter case there is vigorous polymerization of vinyl ether and decomposition of diketene to acetone. Thus, these reactions cannot explain the formation of 2-(1'-ethoxy)ethylacetoacetic ester (I).

The formation of 1,1,3-triethoxybutane (II) by the reaction of diketene and acetal is extremely interesting. It is readily seen that this product could only be formed by dimerization of the starting acetal under the action of boron trifluoride. Despite the fact that the possibility of such dimerization under the action of catalysts has been reported previously in a patent [3], we considered it necessary to study it in more detail as it is of great independent interest. It was found that under the conditions we developed (see experimental section) with BF_3 or a mixture of BF_3 and $ZnCl_2$ as the catalyst, acetal is dimerized in up to 40% yield (on the acetal reacting) to form 1,1,3-triethoxybutane (II), whose structure was readily demonstrated by its conversion to crotonaldehyde 2,4-dinitrophenylhydrazone.

$$2CH_3CH(OC_2H_5)_2 \rightarrow CH_3-\underset{\underset{OC_2H_5}{|}}{CH}-CH_2-CH(OC_2H_5)_2 + C_2H_5OH$$

$$(II)$$

As we showed, in the case of unsaturated acetals, the dimerization may also proceed without the elimination of alcohol. Thus, as a result of addition at the double bond, crotonaldehyde acetal gives up to a 50% yield of 2-(1'-ethoxy)-1,1,3-triethoxy-4-hexene (VI), whose structure was demonstrated by conversion to 2-ethylhexanal, the 2,4-dinitrophenylhydrazone of which did not depress the melting point of an authentic sample.

$$2CH_3CH=CH-CH(OC_2H_5)_2 \rightarrow CH_3-CH=CH-\underset{\underset{OC_2H_5}{|}}{CH}-\overset{\overset{CH_3-CH-OC_2H_5}{|}}{CH}-CH(OC_2H_5)_2$$

$$(VI)$$

Both these modes of dimerization of acetals are of very great interest for the synthesis of polyene compounds.

It was most difficult to isolate and demonstrate the structure of the third product from the reaction of diketene and acetal, which was found to decompose partly even during vacuum distillation; however, we were able to demonstrate that it was the product from the addition of one molecule of diketene to 1,1,3-triethoxybutane (II). (See scheme on next page).

In accordance with the rule established above for the addition of acetal to diketne, it may be considered that this product had structure (III), though the 2,4-dinitrophenylhydrazone obtained from it (m.p. 130-131°) corresponded in analysis to the product from the elimination of one molecule of alcohol (VII). (See scheme on next page).

$$CH_3-C=CH \atop \underset{O-C=O}{\quad}$$

$$+ CH_3-CH-CH_2-CH(OC_2H_5)_2 \atop \underset{OC_2H_5}{\quad} \rightarrow$$
(II)

$$CH_3-C-CH \atop \underset{O}{\overset{\Vert}{}} \quad \underset{COOC_2H_5}{}$$
(III)

with side chain:
$$CH_2-CH-CH_3 \atop CH-OC_2H_5 \; (OC_2H_5)$$

$$CH_3-C-C \atop \underset{O}{\overset{\Vert}{}} \quad \underset{COOC_2H_5}{}$$
(VII)

with:
$$CH_2-CH-CH_3 \atop \underset{CH}{\quad} \; OC_2H_5$$

$$CH_3-C-C \atop \underset{O}{\overset{\Vert}{}} \quad \underset{COOC_2H_5}{}$$
(VIII)

with:
$$CH=CH-CH_3 \atop CH$$

The unsaturated keto ester (VII) could also be obtained in low yield by the direct reaction of diketene with 1,1,3-triethoxybutane and the infrared spectrum confirmed that it had the structure (VII). However, the 2,4-dinitrophenylhydrazone obtained from it had m.p. 185-186° and corresponded in analysis to the 2,4-dinitrophenylhydrazone of the diene keto ester (VIII); its ultraviolet spectrum had λ_{max} 370 mμ (in heptane), which demonstrates that it contained a carbonyl group conjugated with a diene system. All the data examined above show that the product (III) actually has the structure assigned to it.

EXPERIMENTAL

Reaction of diketene with acetal. To a mixture of 41 g of acetal and 5 ml of BF_3 etherate was added a solution of 16.8 g of diketene in 30 g of acetal at such a rate that the temperature did not rise above 40-50°. On the following day the mixture was neutralized with sodium bicarbonate and extracted with ether and the extract dried with magnesium sulfate and distilled. Two successive distillations yielded: 1) 2 g of a fraction with b.p. up to 60° (20 mm) n_D^{20} 1.4022, containing 1,1,3-triethoxybutane (II). The 2,4-dinitrophenylhydrazone obtained from this fraction had m.p. 187-188° and did not depress the melting point of crotonaldehyde 2,4-dinitrophenylhydrazone. 2) 20.4 g of a fraction with b.p. 88-94° (4 mm); n_D^{20} 1.4306; 3) 8.8 g of a fraction with b.p. 108-118° (3 mm); n_D^{20} 1.14418. Fraction 2 was redistilled to yield 19.7 g of 2-(1'-ethoxy)ethylacetoacetic ester (I) with b.p. 84-85° (3 mm); n_D^{21} 1.4292. Found: C 59.73; 59.81; H 8.83; 8.77; (OC_2H_5) 42.5%. $C_{10}H_{18}O_4$. Calculated: C 59.38; H 8.97; (OC_2H_5) 44.6% *.

The 2,4-dinitrophenylhydrazone obtained from (I)** (orange needles with m.p. 163-164° from alcohol) did not depress the melting point of ethylideneacetoacetic ester 2,4-dinitrophenylhydrazone (IV) [5]. Found: C 50.31; 51.21; H 4.91; 5.04; N 17.17; 17.18%. $C_{14}H_{16}N_4O_6$. Calculated: C 50.00; H 4.80; N 16.66%.

Fraction 3 changed on redistillation and we could only isolated from it a small amount of a product with b.p. 80-81° (1 mm); n_D^{20} 1.4482, which corresponded in analysis to 2-(1',3'-diethoxy)butylacetoacetic ester (III). Found: C 61.33; 61.45; H 8.76; 8.70; (OC_2H_5) 46.9%. $C_{14}H_{26}O_5$. Calculated: C 61.29; H 9.55; (OC_2H_5) 49.2%.

After chromatography on Al_2O_3, the 2,4-dinitrophenylhydrazone obtained from this fraction had m.p. 131-132° (from ligroin—benzene) and corresponded in composition to the 2,4-dinitrophenylhydrazone of (VII); λ_{max} 355 mμ (in heptane). Found: C 52.46; 52.55; H 5.60; 5.77%. $C_{18}H_{24}N_4O_7$. Calculated: C 52.80; H 5.86%.

Acid hydrolysis of 2-(1'-ethoxy)ethylacetoacetic ester (I). A mixture of 16 g of 2-(1'-ethoxy)ethylacetoacetic ester (I) and 50 ml of 2 N HCl was heated at 60° for 18 hr. The mixture was neutralized with bicarbonate and carefully extracted with ether (in a percolator). The ether layer was dried and distilled. We isolated 2.5 g of a substance with b.p. 68—85°, from which we obtained a 2,4-dinitrophenylhydrazone with m.p. 159-160° (from

* It has been found [4] that the normal method of analysis for ethoxyl groups gives an error of 2-3% with a similar type of compound. This was confirmed by a special series of analyses, that were kindly carried out by N. L. Shitikova.

** The 2,4-dinitrophenylhydrazones of the ethoxy derivatives precipitated from 2 N HCl as oils. To obtain crystals, it was necessary to extract with ether, dry with $MgSO_4$, and distill the ether from the extract. If this was insufficient it was necessary to use chromatography on Al_2O_3.

ethyl acetate) that did not depress the melting point of ethylideneacetone (V) 2,4-dinitrophenylhydrazone [6]. Found: N 20.80; 20.85%. $C_{11}H_{12}N_4O_4$. Calculated: N 21.22%.

In addition to ethylideneacetone, redistillation of the higher-boiling fractions yielded 3.1 g of ethylidene-acetoacetic ester (IV) with b.p. 86-88° (7 mm); n_D^{20} 1.4474 [2]. Found: C 61.44; 61.39; H 8.07; 8.07%. $C_8H_{12}O_3$. Calculated: C 61.52; H 7.75%. The 2,4-dinitrophenylhydrazone obtained from it had m.p. 161-162° (from alcohol) and did not depress the melting point of an authentic sample.

Preparation of 2-(1'-ethoxy) ethylacetoacetic ester (I). To a mixture of 26 g (0.2 mole) of acetoacetic ester and 70.8 g (0.6 mole) of acetal was added 5 ml of BF_3 etherate and the reaction mixture left at room temperature for a day. The reaction product was neutralized with solid sodium bicarbonate, filtered, and distilled. We isolated 38.8 g of the starting acetal and 12.0 g of acetoacetic ester. Two distillations of the residue yielded 15.9 g of 2-(1'-ethoxy) ethylacetoacetic ester (I) with b.p. 70-73° (1.5 mm); n_D^{20} 1.4276 which represents 78% on the acetoacetic ester reacting. The 2,4-dinitrophenylhydrazone obtained from it had m.p. 163-165° and did not depress the melting point of ethylidene-acetoacetic ester 2,4-dinitrophenylhydrazone. In addition to this dinitrophenylhydrazone, we also isolated a small a-mount of an isomeric 2,4-dinitrophenylhydrazone as yellow needles with m.p. 121-122° (from alcohol), the ultraviolet spectrum of which showed the absence of conjugation (λ_{max}346mμ). Found: C 50.05; 49.85; H 4.73; 4.60%. $C_{14}H_{16}N_4O_4$. Calculated: C 50.00; H 4.80%.

Dimerization of acetal. A mixture of 35.4 g of acetal, 3 g of anhydrous $ZnCl_2$, and 3 ml of BF_3 etherate was left at room temperature for three days and then neutralized with dry sodium bicarbonate, filtered, and distilled. We isolated 6.6 g of the starting acetal, 7.1 g of 1,1,3-triethoxybutane (II) with b.p. 68-73° (8 mm); n_D^{20} 1.4062 [7] and 4.3 g of higher-boiling products. The 1,1,3-triethoxybutane obtained was characterized as crotonaldehyde 2,4-dinitrophenylhydrazone with m.p. 186-188° (λ_{max} 355 mμ), which did not depress the melting point of an authentic sample. In addition to this dinitrophenylhydrazone, we were able to isolate a very small amount of 3-ethoxybutyraldehyde 2,4-dinitrophenylhydrazone as fine golden platelets with m.p. 79-80° (from aqueous alcohol). Found: C 48.15; H 5.53%. $C_{12}H_{16}N_4O_5$. Calculated: C 48.64; H 5.44%.

Dimerization of crotonaldehyde acetal. To 14.4 g of crotonaldehyde acetal was carefully added 0.5 ml of BF_3 etherate with cooling. After the vigorous reaction, the mixture was neutralized with sodium bicarbonate, filtered, and distilled. Two distillations yielded 7.3 g of the dimer (VI) with b.p. 105-108° (3 mm); n_D^{17} 1.4366. Found: C 66.40; 66.64; H 10.83; 10.80; (OC$_2$H$_5$) 59.3%. ($C_8H_{16}O_2$). Calculated: C 66.63; H 11.18; (OC$_2$H$_5$) 62.6%.

Reaction of diketene with 1,1,3-triethoxybutane (II). To a mixture of 7.6 g (0.08 mole) of diketene and 15.5 g (0.08 mole) of 1,1,3-triethoxybutane was added 3 ml of BF_3 etherate at such a rate that the temperature did not rise above 30°. After 2 hr, the reaction product was neutralized with dry sodium bicarbonate, filtered, and distilled. We obtained 3.4 g of acetoacetic ester (confirmed by preparation of the 2,4-dinitrophenylhydrazone) and 8.5 g of a fraction with b.p. 94-140° (1.5 mm); n_D^{20} 1.4502; two distillations of the latter yielded a product with b.p. 87-91° (1 mm); n_D^{20} 1.4626, which corresponded in analysis to the substance (VII). Found: C 62.73; 62.68; H 8.59; 8.66%. $C_{12}H_{20}O_4$. Calculated: C 63.2; H 8.76%.

The infrared spectrum of this compound had absorption bands at 1640 and 1725 cm^{-1}, which confirmed that it contained carbonyl and carboxyl groups conjugated with a double bond. The 2,4-dinitrophenylhydrazone obtained from it formed dark red needles with m.p. 185-186° (from alcohol) and corresponded in analysis to the 2,4-dinitrophenylhydrazone of the diene keto ester (VIII), as was confirmed by the ultraviolet spectrum: λ_{max}370 mμ (in heptane). Found: 52.88; 53.12; H 5.06; 5.28%. $C_{16}H_{18}N_4O_6$. Calculated: C 53.1; H 4.96%.

SUMMARY

1. The reaction of acetal with diketene in the presence of BF_3 etherate gives as the main product 2-(1'-ethoxy)ethylacetoacetic ester (I). 1,1,3-Triethoxybutane (II) and 2-(1',3'-diethoxy) butylacetoacetic ester (III) are formed as by-products.

2. The reaction of acetal with acetoacetic ester was studied and found to give a good yield of 2-(1'-ethoxy) ethylacetoacetic ester (I).

3. On the example of acetaldehyde and crotonaldehyde acetals it was shown that acetals may be dimerized to compounds which could be of interest for the synthesis of polyene compounds.

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CATALYTIC DEHYDRATION OF α-ISOBUTYLTETRAHYDROFURAN

N. I. Shuikin and G. K. Vasilevskaya

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

The catalytic dehydration of tetrahydrofuran homologs for preparing dienes has been studied mainly with tetrahydrosylvan. The dehydration of tetrahydrofuran and tetrahydrosylvan over the acid catalysts NaH_2PO_4, Ca $(H_2PO_4)_2$, and a mixture of boric and phosphoric acids [1] gave butadiene and piperylene, respectively, in high yields up to 88-91% [2]. Some authors [2, 3] have reported that carrying out the dehydration at low pressure (30 mm Hg) leads to an increase in the diene yield. In the work of Shuikin, Tulupov, and Bel'skii [3] on the dehydration of tetrahydrosylvan over a titanium—alumina catalyst at 500-600° and a pressure of 20-30 mm it was found that this catalyst promotes the formation of dienes of both open and cyclic structure. In addition, the authors concluded that cyclopentadiene is formed directly from tetrahydrosylvan and the dehydration of the latter to piperylene proceeds independently, in parallel. By dehydrating ethyltetrahydrofuran under the same conditions, Shuikin and Bel'skii [4] obtained a mixture of dienes in 66% yield from which they isolated, in addition to dienes of open structure, β-methylcyclopentadiene and 1,3-cyclohexadiene and also benzene, which was apparently formed by dehydrogenation of the latter.

We studied the dehydration of a more complex homolog of tetrahydrofuran, namely, α-isobutyltetrahydrofuran. In carrying out this reaction over a titanium-alumina catalyst, we expected the formation of a mixture of dienes, consisting of 6-methyl-1,3-heptadiene and its dehydrocyclization products. However, when treated at 600 and 550°, a pressure of 20-30 mm, and a space velocity of 0.1 hr^{-1}, the α-isobutyltetrahydrofuran underwent deep cracking to a considerable extent so that we obtained liquid catalyzates in a yield of only 25-30%; they were a complex mixture of high-boiling hydrocarbons, that resinified rapidly. Then by lowering the temperature to 400° and reducing the contact time, we obtained a liquid catalyzate in 95% yield; it contained from 81.0 to 92% of dienes in separate fractions boiling over the range 121.7-136°.

Thus, by starting from pentosan-containing raw material and passing through the stages of furfural, furan homologs, and their tetrahydro derivatives, it is possible to obtain considerable amounts of unsaturated hydrocarbons, in particular, dienes. The next problem is to find conditions for directing the course of the catalytic dehydration of tetrahydrofuran homologs to form a less complex mixture of dienes and alkenes so that individual hydrocarbons can be isolated.

EXPERIMENTAL

The starting α-isobutyltetrahydrofuran was synthesized according to the following scheme:
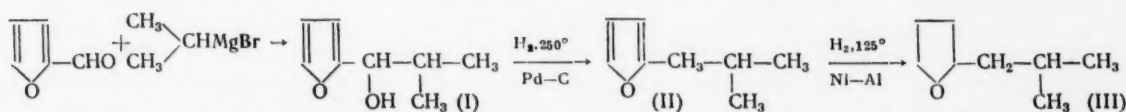
Isopropylfurylcarbinol (I) had b.p. 88-90° (17 mm); n_D^{20} 1.4777 and d_4^{20} 1.0310 [5]. It was then hydrogenated selectively over palladized charcoal at 250° to α-isobutylfuran (II) by the method proposed by Shuikin and Bel'skii [5] for alcohols of the furan and benzene series. α-Isobutylfuran was obtained in 65% yield and had b.p. 128° (746 mm); d_4^{20} 0.8784 and n_D^{20} 1.4420 [5]. α-Isobutylfuran was then hydrogenated to α-isobutyltetrahydrofuran (III) over a skeletal nickel-aluminum catalyst at 125°. The α-isobutyltetrahydrofuran, which was obtained in practically quantitative yield, boiled at 148-149° (746 mm) and had n_D^{20} 1.4265 and d_4^{20} 0.8484 [5].

The catalyst for the dehydration of α-isobutyltetrahydrofuran was prepared by carefully grinding titanium dioxide with 5% of moist alumina in a mortar. The mixed was then formed into tablets and fired at 600° for 3 hr.

α-Isobutyltetrahydrofuran was dehydrated at 400° and a pressure of 25-30 mm with a space velocity of 0.25-0.30 hr^{-1}; it was passed in 50 g portions and then the catalyst was regenerated by oxidation in a stream of air at 550-600° for 2 hr. The yield of the wet catalyzate was 95% and after removal of the water, 78%. The catalyzate was dried and distilled on a column with an efficiency of 40 theoretical plates. The results of fractionation are given in the table.

Properties of Fractions Isolated by Distilling Dehydration Products of α-Isobutyltetrahydrofuran

Fraction no.	B.p. in °C at 746 mm	n_D^{20}	d_4^{20}	Bromine number	Content, % dienes	Content, % alkenes	Yield in g	Yield in % on catalyzate
I	63—84	1,3926	0,7111	128	10,7	55,4	2,05	2,7
II	84—91	1,4003	0,7071	135,8	2,6	68,2	4,24	5,4
III	91—96	1,4060	0,7140	129,6	8,2	69,5	1,45	1,9
IV	96—112	1,4150	0,7335	147,7	3,3	84,2	7,01	9,0
V	112—114	1,4145	0,7605	133,6	30,9	44,7	2,88	3,7
VI	114—117	1,4161	0,7231	125,7	28,0	54,4	4,36	5,7
VII	117—121,7	1,4253	0,7488	167	29,0	70,1	6,73	8,7
VIII	121,7—125	1,4387	0,7764	151,5	91,5	—	11,27	14,4
IX	125—130	1,4473	0,7737	194,5	92,0	—	4,88	6,3
X	130—136	1,4628	0,7733	142,6	81,0	—	11,59	14,8
XI	136—150	1,4587	0,8227	65,4	12,0	31,1	7,38	9,5
XII	Tarry residue	—	—	—	—	—	10,0	13,0

The diene content of each fraction was determined by the method of Kaufmann et al. [6]. For this purpose, a sample of the substance was heated under reflux for 8 hr with excess maleic anhydride; the unreacted maleic anhydride was then dissolved in water and the maleic acid titrated with 0.1 N sodium hydroxide solution. The alkene content of the fractions was determined by the Kaufmann-Gal'pern method [7]. The content of alkenes, present simultaneously with dienes, was calculated by the formula presented in the work of Timofeeva, Kleimenova, and Dobrynina [8]:

$$H = \frac{NM}{160} - 1,2D,$$

where H is the alkene content in weight %, N is the bromine number, M is the molecular weight of the alkene, D is the diene content in weight %, and 1.2 is an empirical coefficient.

From the properties of fractions VII and VIII it may be concluded that they contained 6-methyl-1,3-heptadiene, which should be the main dehydration product of α-isobutyltetrahydrofuran. In a report published in 1896 [9], only b.p. 116-118° and d_{22} 0.741. were given for this diene. However, it should be remembered that these fractions could also have contained the corresponding 6-methylheptenes (hydrogen disproportionation products) and also dimethylcyclohexadiens and dimethylcyclohexenes. It is probable that cyclic dienes were present in fractions VIII and IX. It was impossible to isolate them by fractionation. As the data presented show, the dehydration of α-isobutyltetrahydrofuran under the conditions adopted was accompanied by hydrogen disproportionation and this resulted in alkenes and cyclenes appearing in the catalyzate. We attempted to isolate the alkene formed from these fractions in which their content was sufficiently high. For this purpose, fractions IV and VII were heated

under reflux for 8 hr with two equivalents of maleic anhydride relative to the dienes in these fractions. The mixture, containing excess maleic anhydride, alkenes, and the adducts of dienes and maleic anhydride, was filtered to remove the latter; the alkenes were washed carefully with 10% sodium carbonate solution to remove maleic anhydride, dried with calcium chloride, and distilled over sodium.

The alkenes from fraction IV had b.p. 96-104° (750 mm); n_D^{20} 1.4140 and d_4^{20} 0.7127; this mixture apparently contained 3-heptene [9] and some methylcyclohexenes. The alkenes from fraction VII with b.p. 116-118° (748 mm) had n_D^{20} 1.4234 and d_4^{20} 0.7426; this mixture contained 6-methyl-3-heptene [9], probably with some dimethylcyclohexene. Fraction XI was treated with sulfuric acid until the unsaturated hydrocarbons had been removed completely and the residue (4.1 g) was washed with water and dried with calcium chloride. When distilled over sodium, it boiled at 146-148° (740 mm); judging by its properties (n_D^{20} 1.4272 and d_D^{20} 0.8490), this substance was unchanged α-isobutyltetrahydrofuran.

SUMMARY

1. Dehydration of α-isobutyltetrahydrofuran over a titanium-alumina catalyst at 400°, a pressure of 20-30 mm, and a space velocity of 0.25-0.30 hr^{-1} yielded a catalyzate containing up to 92% of dienes in fractions boiling over the range 121.7-128°.

2. Simultaneously with dehydration of α-isobutyltetrahydrofuran, there was disproportionation of hydrogen among the reaction products, resulting in the formation of C_7-C_8 alkenes.

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THE EFFECT OF THE MEDIUM ON THE COURSE
OF OXIDATIVE FISSION OF n-BUTYLBENZENE
AND TOLUENE

D. I. Dimitrov

The Chemico-Technological Institute, Sofia, Bulgaria

It was shown in a previous paper [1] that, in the oxidation of n-butylbenzene and n-amylbenzene with alkaline potassium permanganate, the side chain was broken between the α- and β-carbon atoms, the products being benzoic acid and propionic or butyric acid accordingly. The resulting fatty acids can be oxidized in turn to acetic acid [2,3]. Propionic acid was also found in the oxidation product from amylbenzene. It might therefore be supposed that rupture of the side chain also occurred in a diffferent position to that indicated above. There is very little information in the literature on the behavior of alkylbenzenes with longer side chains under the conditions of oxidation by potassium permanganate. Rupture between the α- and β-carbon atoms of the side chain is generally considered the most probable. It is also generally accepted that potassium permanganate does not break open the aromatic nucleus of benzene hydrocarbons. However, Cullis and Ladbury observed splitting of the aromatic rings of xylenes [4] under the action of potassium permanganate in 54.2% acetic acid; such splitting was not observed with toluene [5], ethylbenzene [6], and isopropylbenzene [7], but they considered that it was possible.

In this paper I have considered the behavior of the benzene ring and of the alkyl side chains of aromatic hydrocarbons during oxidation, on the basis of a study of the compositions of the acids obtained by oxidizing n-butylbenzene and toluene with a solution of potassium permanganate in the following media: a) N sulfuric, b) M phosphate buffer of pH 7, c) M phosphate buffer of pH 10, d) N sodium carbonate, e) N potassium hydroxide.

EXPERIMENTAL

n-Butylbenzene was prepared from n-bromobutane and bromobenzene by the action of sodium [8]. All the reagents, including toluene, were of "pure for analysis" grade. The buffer solutions were obtained by mixing M solutions of KH_2PO_4 and NaOH in the appropriate proportions; the pH was checked with universal indicator.

In performing the experiments, a mixture of 0.5 ml of n-butylbenzene or toluene with 100 ml of potassium permanganate solution in one of the above media was mixed with a mechanical stirrer at a temperature and for a time shown in Tables 1 and 2. The excess unreacted permanganate was then immediately decomposed by addition of oxalic acid. Excess of unreacted oxalic acid was then removed by addition of a little permanganate solution until a permanent brown precipitate was obtained. This precipitate was filtered off and the solution was extracted with ether continuously for 8 hours. The ether extract was dried and the ether distilled off, the residue was treated, drop by drop, with 0.5 ml of 25% ammonia solution, excess ammonia and residual ether was evaporated off, and the resulting solution of ammonium salts was filtered into a glass ampule for storage.

The solutions of the ammonium salts were analyzed for monocarboxylic organic acids by chromatography on Whatman No. 1 paper, using 1.5 N ammonia in n-butanol as solvent, in the usual way [9]. All the analyses were made by the descending method. The acid spots were detected by means of the indicator Methyl Red [10]. The acids were mostly identified by comparison with standards. The observed Rf values, in general higher than the

TABLE 1

Oxidation of n-Butylbenzene

Experiment No.	Experimental conditions			Presence of unreacted n-butylbenzene	Acids found			
	Medium for oxidation	Temp. °C	Time of expt. min.		Acetic	Pro-pionic	Buty-ric	Ben-zoic.
1	6% KMnO$_4$ in N H$_2$SO$_4$	30	30	Yes	+	+	+	+
2	The same	30	45	"	+	+	+	+
3	The same	30	145	No	+	+		+
4	" "	80	60	"	+	+	+	+
5	4% KMnO$_4$ in M phosphate buffer of pH 7	80	85	"	+	+		+
6	4% KMnO$_4$ in M phosphate buffer of pH 10	80	85	Yes	+	+		+
7	4% KMnO$_4$ in N Na$_2$CO$_3$	30	10	"	+			
8	4% KMnO$_4$ in N KOH	30	90	?	+		+?	
9	The same	30	30	Yes	+?			+

TABLE 2

Oxidation of Toluene

Expt. No.	Experimental conditions		Duration of oxidation, min	Presence of unreacted toluene after experiment	Acids found	
	Medium for oxidation	Temperature °C			acetic	benzoic
10	4% KMnO$_4$ in N H$_2$SO$_4$	30	45	Yes	+	+
11	The same	30	150	"	+	+
12	4% KMnO$_4$ in M phosphate buffer of pH 7	30	30	"	+?	+
13	4% KMnO$_4$ in M phosphate buffer of pH 10	30	30	"	+?	+
14	4% KMnO$_4$ in N Na$_2$CO$_3$	30	300	"	"	+
15	4% KMnO$_4$ in N KOH	30	30	"		+

literature values, were as follows: acetic acid 0.13, propionic acid 0.23, n-butyric acid 0.36, benzoic acid 0.45, and n-valeric acid 0.52. The results are shown in Tables 1 and 2.

The marked effect of the medium on the composition of the acids obtained by n-butylbenzene oxidation is clear from Table 1 and Fig. 1*. Three different types of behavior were observed.

1. Oxidation of n-butylbenzene in N sulfuric acid. The acid spots showed that the primary oxidation products were only n-valeric, n-butyric, and benzoic acids, and part of the propionic acid. The individual experiments showed that n-butyric acid was not an oxidation product of n-valeric acid. Propionic acid was a primary product, since it was formed simultaneously with benzoic acid, but it was also formed as a secondary product of the β -oxidation of n-valeric acid [2]. Acetic acid was probably formed by the β -oxidation of n-valeric and n-butyric acids [2], and also by the oxidation of propionic acid [3].

On the basis of the above it may be concluded that, when n-butylbenzene is oxidized in N sulfuric acid, it splits up in at least three ways: a) splitting of the aromatic ring to give n-valeric acid; b) splitting between the aromatic ring to give n-valeric acid; b) splitting between the aromatic ring and the side chain to give n-butyric acid; c) splitting between the α- and β -carbon atoms of the side chain to give benzoic and propionic acids. The oxidation process should be as short as possible in order to observe all three forms of splitting. Otherwise, the n-

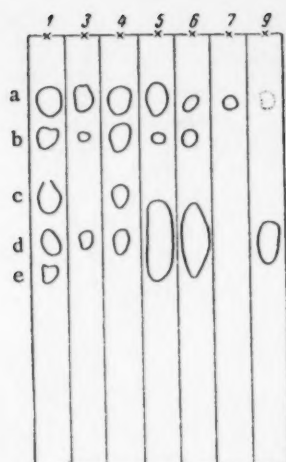* The chromatogram numbers correspond to the experiment numbers

Fig. 1. Chromatograms of the
oxidations products of n-butyl-
benzene: a) acetic acid, b)
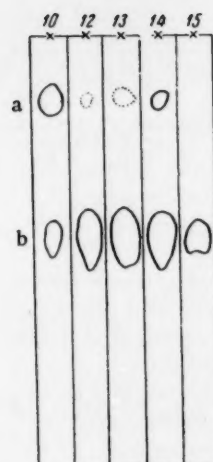propionic acid, c) butyric acid,
d) benzoic acid, e) valeric acid.

Fig. 2. Chromatograms
of the oxidation products
of toluene: a) acetic acid,
b) benzoic acid.

valeric acid (experiment 4) and the n-butyric acid (experiment 3) are further oxidized to lower products and can no longer be detected.

2. Oxidation of n-butylbenzene in M phosphate buffer solutions. The results were in agreement with those described in the previous paper [1]. Splitting only occurred between the α- and β-carbon atoms. The acetic acid formed was a secondary product of oxidation of propionic acid. The results obtained with N KOH belong to the same group. The benzoic acid formed in this case (experiment 9) showed that splitting occurred only, or mainly, between α- and β-carbon atoms. The vanishingly small amount of acetic acid and the absence of propionic acid were due to the almost complete oxidation of the latter [3]. The results with media of pH 7 and 10 were quite different to those of experiment 4 with a medium of pH 1. It is clear from Fig. 1 that the benzoic acid spots in the chromatograms of the products from media of pH 7 and 10 were considerably larger than the acetic acid spots. On the other hand, these spots were of almost equal area in the chromatograms from experiment 4. The results from experiments with media of pH 7 and 10 were in agreement with the assumption that splitting occurred mainly between the α- and β-carbon atoms.

3. Oxidation of n-butylbenzene in N sodium carbonate solution. Acetic acid was the only acid detected in the oxidation products. The absence of benzoic acid inidcated that fission did not occur between the α- and β-carbon atoms. The presence of acetic acid was obviously due to primary production of n-butyric or n-valeric acids, whose rate of further oxidation was more rapid than the rate of heterogeneous oxidation of n-butylbenzene in this medium. The results of toluene oxidation (Table 2 and Fig. 2) confirmed the possibility of splitting of the aromatic ring. In a sodium carbonate medium, the oxidation of toluene differed from that of n-butylbenzene in that benzoic acid was found with acetic acid in the oxidation products. This can be explained by differences in the rates of oxidation of the intermediate [4-7] α-carbonyl compounds:

$$C_6H_5-CH_3 \rightarrow C_6H_5CHO$$
$$C_6H_5-CH_2-CH_2-CH-CH_3 \rightarrow C_6H_5-CO-CH_2CH_2-CH_3$$
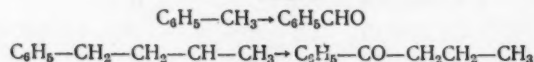
Oxidation of benzaldehyde to benzoic acid occurs readily, and its rate is probably higher than the rate of rupture of the bonds between an aromatic ring and a side chain. On the other hand, oxidation of propyl phenyl ketone is only possible with rupture of one or both of the carbon bonds to the carbonyl group. The results obtained agree satisfactorily with the assumption of splitting of the bond between the aromatic ring and the side chain of propyl phenyl ketone.

SUMMARY

1. A study has been made of the effect of the medium on the direction of the oxidative splitting of n-butyl-benzene and toluene by potassium permanganate.

2. Oxidative splitting of the side chain is also accompanied by fission of the aromatic ring.

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REACTIONS OF FREE RADICALS IN SOLUTION

17. THE EFFECT OF THE VISCOSITY OF THE MEDIUM ON THE PRIMARY RECOMBINATION OF FREE RADICALS

B. L. Erusalimskii, A. P. Kavunenko, and B. A. Dolgoplosk

The Institute for High Molecular Compounds of the Academy of Sciences of the USSR

It is known that, in the thermal decomposition of methylphenyltriazen in saturated hydrocarbon solution, the main products in addition to the nitrogen evolved quantitatively, are methane and methylaniline:

$$C_6H_5NHN=NCH_3 \nearrow^{CH_4} \searrow_{C_6H_5NHCH_3}$$
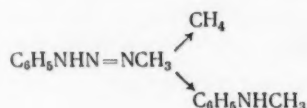
It is most probable that methylaniline is formed by primary recombination of the free radicals $CH_3\cdot$ and $C_6H_5NH\cdot$. A point in favor of this assumption is that the yield of alkylanilines in the decomposition of various alkylaryltriazens is independent of the reactivities of the alkyl free radicals, produced by the decomposition of the triazens [1].

In a previous paper [2] we presented preliminary data showing that, when methylphenyltriazen was decomposed in a hydrocarbon-polymer system, the methane yield decreased with increasing viscosity of the medium. It was also found that there was a marked increase in the methylaniline yield when the decomposition was carried out in a medium of very high viscosity. These results indicated that the viscosity of the medium affected the extent of the reaction of primary recombination of free radicals. The object of the present paper was to investigate the thermal decomposition of methylphenyltriazen in a cymene-polystyrene system, and to find the effects of molecular weight and concentration of polymer on the methane and methylaniline yields. We found that, when the reaction was carried out in solutions containing 60% of polystyrene of molecular weight varying from 5000 to 200,000, there was practically the same decrease in methane yield as compared with the reaction in the pure solvent. However, this was not associated with any increase in the methylaniline yield, which remained the same as in the absence of polymer. The methylaniline yield only increased significantly, and was accompanied by a marked fall in the methane yield (Table 1), when the molecular weight of the polystyrene was 600,000 and its concentration in solution was maintained at 60%.

It follows from this that the change in methane yield, in solutions containing polystyrene of molecular weight up to 200,000, cannot be attributed to an increase in the viscosity of the medium, or it would inevitably be accompanied by an increase in the yield of the primary recombination product, namely methylaniline. The decreased methane yields in experiments 2-4 must therefore be attributed to a difference between the relative activities of polystyrene and cymene as hydrogen donors; this explanation is in accordance with literature data on the lower

mobility of hydrogen atoms in polystyrene, as compared with cymene [3]*. It also fits in with the results obtained for the methane yields in systems containing much lower polystyrene concentrations. We found that, under such conditions, there was a decrease in methane yield which depended only on the polymer concentration, and not on its molecular weight (Table 2).

TABLE 1

Yields of the Main Conversion Products of Free Radicals in the Thermal Decomposition of Methylphenyltriazen in the System Cymene-Polystyrene at 110°

Expt. no.	Polystyrene		Yield, %theoretical			
	mol.wt.	concn. % w/w	methane	total amines	aniline	methyl-aniline
1	—	—	51,3	84,0	62,0	22,0
2	5000	60	30,5	undetermined		
3	80000	60	28,8	81,0	56,0	25,0
4	200000	60	29,5	83,3	59,5	23,8
5	600000	60	13,6	89,0	53,0	36,0

TABLE 2

Methane Yields in the Thermal Decomposition of Methylphenyl-triazen in the System Cymene-Poystyrene at 110°

Polystyrene mol. wt.	Polystyrene concn., % w/w	Methane yield, % theor.
5 000	5	49,2
600 000	5	50,5
5 000	20	40,3
600 000	20	40,5

On the other hand, the results for very viscous systems (Table 1, experiment 5) show clearly that the diffusion rate of free radicals from the micelles was considerably reduced, and this led to a marked increase in the part played by the primary recombination reaction.

EXPERIMENTAL

The experiments were carried out in ampules, fitted with an inlet tube and an outlet connected to a gas buret. After completion of the triazen decomposition, which took 8-9 hours, water was added through the tube and the ampule was heated by steam to remove gas "entrained" in the polymer. The methane was determined by combustion of a gas sample over copper oxide.

In order to determine the amines in the reaction mixture after the methylphenyltriazen decomposition, kerosine (b.p. 170-200°) was added so that the amines could be distilled off completely. The ratio of aniline to methylaniline in the kerosine distillate was determined by the Shchetinin method [5]. The methods for determining methane and amines required different treatments of the reaction mixture, so that, in order to establish the yields of these products, it was necessary to carry out separate experiments under identical conditions. Data for two typical experiments was as follows: a) Methylphenyltriazen (0.259 g) was decomposed at 110° in a solution containing 2.2 g of cymene and 3.3 g of polystyrene of molecular weight 80,000. The volume of gas collected was 73 ml at N.T.P. The methane content of the gas was 16.4%, so that the methane yield was 28.1% theoretical. b) Methylphenyltriazen (2.114 g) was decomposed at 110° in a solution containing 20 g of cymene and 30 g of polystyrene (mol. wt. 80,000). The mixed amines were extracted from the kerosine with concentrated hydrochloric acid. Titration of iodine, after treatment of an aliquot portion of the hydrochloric acid solution by the bromide-bromate method, was equivalent to 256.6 ml of 0.1059 N thiosulfate for the whole sample, corresponding to a total amine yield of 81.0% theoretical. Diazotization of an aliquot portion gave a volume of nitrogen equivalent to 198.7 ml at N.T.P. for the whole sample. The aniline yield was therefore 56.0% theoretical, and the methylaniline yield (by difference) 25% theoretical.

SUMMARY

1. An investigation has been made of the yields of methane and methylaniline formed by the thermal decomposition of methylphenyltriazen in the system cymene-polystyrene, as a function of the concentration and molecular weight of the polymer.

2. In very viscous systems there is a considerable increase in the role of the primary recombination of free radicals, and this leads to an increase in the methylaniline yield and a simultaneous decrease in the methane yield.

*It follows that there must here be a considerable combination of free methyl radicals with the aromatic ring, which is known to occur to a significant extent under certain conditions [4]. A similar assumption is necessary to explain the general decrease in the CH_3·radical balance in experiments 3 and 4.

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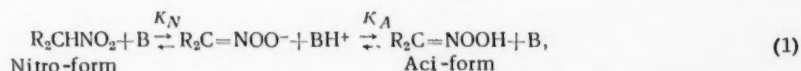

THE TAUTOMERISM OF NITROCOMPOUNDS

1. INVESTIGATION OF THE MECHANISM OF THE TAUTOMERIC TRANSFORMATIONS OF PHENYLNITROMETHANE

V. M. Belikov, S. G. Mairanovskii, Ts. B. Korchemnaya, S. S. Novikov, and V. A. Klimova

The tautomerism of aliphatic nitrocompounds has attracted the attention of numerous investigators. This is not surprising, since elucidation of the mechanism of tautomeric conversions is one of the cardinal problems of organic chemistry—the problem of the dual reactivity of organic compounds. Nowadays, in accordance with the general principle of protolytic equilibrium the following scheme is used for the tautomeric conversions of nitrocompounds (see [1] for example):

$$\underset{\text{Nitro-form}}{R_2CHNO_2 + B} \overset{K_N}{\rightleftharpoons} R_2C=NOO^- + BH^+ \overset{K_A}{\rightleftharpoons} \underset{\text{Aci-form}}{R_2C=NOOH + B}, \tag{1}$$

where B is a base, and K_N and K_A are the dissociation constants of the nitro- and aci-forms respectively. This scheme only gives a simplified representation of the process and leads to a number of inconsistencies. In order to apply this scheme we are forced to accept a number of assumptions which are not in accordance with the experimental facts.

All investigators studying the isomerization of the aci-form into the nitro-form have assumed: a) that only one anion $RCH=NOO^-$, the same for the aci- and the nitro-forms, participates as a kinetic stage in the equilibrium; b) that equilibrium between the aci-form and its anion is established instantaneously, so that dissociation of the aci-form cannot be a rate determining stage in the isomerization of the aci- to nitro-form. The rate determining stage is taken to be the recombination of the anion with a proton to give the nitro-form. It should be noted that this assumption has often been queried, but no experimental work has been done to check it. The only work directed to the elucidation of this problem is that of Maron and La Mer [1]. However, these authors misinterpreted their experimental results, as was shown subsequently by Pearson and Dillon [2].

Inconsistencies in scheme (1) arise, for example, in attempts to correlate the acidity of a mononitroalkane with the nature of the alkyl substituent. Thus, in the series CH_3NO_2, $CH_3CH_2NO_2$, and $(CH_3)_2CHNO_2$, it would be expected, on the basis of the inductive effect of the methyl group, that the ease of dissociation of the nitro-form to give the anion $R_2C=NOO^-$ [equation (1)] would decrease, and, consequently, that the acidity would decrease from nitromethane to nitroethane, and again to 2-nitropropane. In fact, the reverse was found. In order to explain this anomaly, Turnbull and Maron [3] adopted the hypothesis, put forward by Pederson [4] and Junell [5], that there is a second anion in equilibrium with the aci-form anion. According to this assumption, equation (1) should have the form:

$$R_2CHNO_2 + B \xrightleftharpoons[k_{NR}^{BH^+}]{k_{ND}^{B}} R_2C^-NO_2 + BH^+ \xrightleftharpoons[k_2]{k_1} R_2C=NOO^- + BH^+ \xrightleftharpoons[k_{AD}^{B}]{k_{AR}^{BH^+}} R_2C=NOOH + B$$
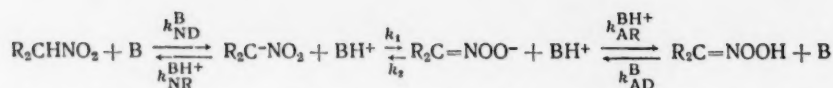
The indices to the constants k have the following meanings: A and N refer to the aci- and nitro-forms respectively; D and R refer to the dissociation and recombination reactions; B and BH$^+$ denote the base and acid respectively, and the velocity constants refer to reactions with these.

The dissociation constants may be written:

$$K_N = \frac{[R_2C=NOO^-][H_3O^+]}{[R_2CHNO_2]}$$

$$K_N' = \frac{[R_2C^-NO_2][H_3O^+]}{[R_2CHNO_2]} = \frac{k_{ND}^{H_2O}}{k_{NR}^{H_2O^+}}[H_2O]$$

$$K_A = \frac{[R_2C=NOO^-][H_3O^+]}{[R_2C=NOOH]} = \frac{k_{AD}^{H_2O}}{k_{AR}^{H_2O^+}}[H_2O]$$

These symbols have the same meaning throughout this paper.

Equilibrium between the two anions can be expressed as follows:

$$K = \frac{[R_2C=NOO^-]}{[R_2C^-NO_2]} = \frac{k_1}{k_2}$$

Turnbull and Maron [3] showed that, if K is large, the measured dissociation constant K_N of the nitro-form is related to K_N' by the expression:

$$K = \frac{K_N}{K_N'} - 1 \tag{2}$$

The increased proton affinity resulting from replacement of H by CH_3 in CH_3NO_2 causes a reduction in K_N, and is equivalent to a reduction in the affinity of carbon for an electron; this should make it possible for $R_2C=NOO^-$ to be formed at the expense of $R_2C^-NO_2$, i.e. K should increase. Since the increase in K can outweigh the decrease in K_N' the constant K_N can increase significantly when substitution occurs, as observed in practice.

Another explanation of the effect of substitution on the acidity of nitroalkanes was given by Wheland and Farr [6], who attributed the effect to a difference in the dielectric properties of the medium and the molecule (CH_3 group). This explanation appears highly improbable, since such a difference should be preserved in other homologous series. However, in the 1,1-dinitroalkane series, a reduction in acidity was observed between dinitromethane [7] and 1,1-dinitroethane [8,9].

Thus, we can conclude from the literature data that considerable doubt attaches to the previously accepted assumption that there is only one type of nitrocompound anion. There is also no proof of the other current assumption used in investigating the kinetics of tautomeric transformations in nitrocompounds, namely that the equilibrium between the aci-form and its anion is established instantaneously. On the contrary, some authors [2, 10], in discussing their experimental work on the mechanism of tautomeric transformations in nitrocompounds has been carried out by conductometric or brommometric methods. The use of these methods makes interpretation of the experimental results both difficult and uncertain.

The object of our work was to obtain a more complete picture of these tautomeric transformations by the use of a more correct technique. Polarography was the method selected. This had the advantage that it was possible to determine the concentrations of both nitro- and aci-form of nitrocompound simultaneously; the anions were found to polarographically inactive.

The compound chosen for investigation was phenylnitromethane, which shows relatively slow rates of tautomeric interconversion. Phenylnitromethane is a monobasic acid; under the influence of a bse it dissociates to form an anion and an acid combined with the base. We measured the acid dissociation constant of phenylnitromethane in water (K_N), potentiometrically and polarographically, and found it to be 1.6×10^{-7} mole/liter.

We investigated the kinetics of the dissociation of phenylnitromethane in buffer solutions between pH 7 and 10. Since the observed rate of dissociation included the rates of interaction of $C_6H_5CH_2NO_2$ with water, OH^-, and the base component of the buffer, we determined experimentally the velocity constants for all these components. The rate of interaction with water, selected as a standard base, could not be determined reliably. We therefore obtained an approximate value, by extrapolation from the Bronsted equation (see contribution 2), of $k_{ND}^{H2O} \sim 8 \times 10^{-7}$ liter/mole·sec.

We also studied the kinetics of the transformation of the aci-form into the nitro-form at pH 1 to 6. The measurements were carried out as follows. A precisely measured quantity of an aqueous solution of the phenylnitromethane potassium salt was added to the buffer, whereupon the aci-form was produced immediately and was slowly converted into the nitro-form. It was found that, below pH2 the rate of isomerization did not depend on the hydrogen ion concentration, and corresponded to the rate of interaction of the aci-form with water, in accordance with the equation:

$$C_6H_5CH{=}NOOH + H_2O \xrightarrow{\;k_{AD}^{H_2O}\;} C_6H_5CH{=}NOO^- + H_3O^+$$

However, the rate of isomerization began to increase at higher pH, and the pH at which the increase began depended on the concentration of base in the buffer. With decreasing concentration of this base, the bend in the curve relating isomerization rate and pH shifted to a higher pH. This showed that the isomerization rate was determined by the dissociation of the aci-form stage:

$$C_6H_5CH{=}NOOH + B \xrightarrow{\;k_{AD}^{B}\;} C_6H_5CH{=}NOO^- + BH^+$$
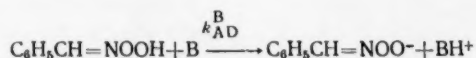
In this case, as in the determination of the dissociation rate of the nitro-form, the constants were determined with all the buffer components. The results obtained for the velocity constant of the reaction agreed well with the Bronsted equation (see next contribution). The aci-form of phenylnitromethane was found to be a stronger acid than the nitro-form. Its dissociation constant K_A was determined potentiometrically and polarographically; $K_A = 1.3 \times 10^{-4}$ mole/liter.

Investigation of the behavior of the phenylnitromethane anion in buffer solutions at pH 4 to 6 showed that, within the pH range 4 to 4.7, the reaction rate for the formation of the nitro-form was practically independent of pH. However, at higher pH, this rate decreased proportionally with the decrease in acid concentration. In this region, the formation rate of the nitro-form was determined by the stage of recombination of anion to give undissociated nitro-form:

$$(C_6H_5CHNO_2)^- + BH^+ \longrightarrow C_6H_5CH_2NO_2 + B$$

The partial rates of this process were found for all the acid components of the buffer, namely H_3O^+, $H_2PO_4^-$ $(CH_3)_3CCOOH$, CH_3COOH, and $ClCH_2COOH$. These partial rates were all in satisfactory agreement with the Bronsted equation (see next contribution).

Thus we determined experimentally the rates of dissociation and recombination of the nitro-form and the rate of dissociation of the aci-form. We could then use our value of the dissociation constant K_A to calculate the rate of recombination of the aci-form, employing the method suggested by Maron and La Mer [3].

The ratio of our observed values of k_{NR} and k_{AR} was not in agreement with the experimental fact that the aci-form was produced when the phenylnitromethane salt was acidified with a strong acid. Actually, if we calculated first order rates for pH 2, it appeared that the nitro-form should be produced ten times as fast as the aci-form. In order to bring our results into line with experiment, we were forced to suppose that there was an intermediate stage, which slowed up the process, in the production of nitro-compound from anion. We therefore assumed

that the anion could exist in two forms, and that this slow stage was the conversion of the aci-anion into the nitro-anion, the velocity constant under these conditions being $2 - 20 \times 10^{-3}$ sec^{-1}. A rate of this order did not conflict with the observation that the isomerization rate at low pH was determined by the dissociation rate of the aci-form. This low value of k_2 could probably be attributed to the change in spatial distribution of atoms in transforming from one type of anion to the other and the associated process of rupture and formation of ion pairs, since the transformation rate evidently depended on the acid concentration in the solution:

$$\left[C_6H_5CH = N \overset{O}{\underset{O}{\big\langle}}\right] \quad H_3O^+ \quad \overset{k_2}{\to} \quad C_6H_5CH-N \overset{O}{\underset{O}{\big\langle}} \quad + \quad H_3O^+$$
$$\underset{H_3O^+}{\big\uparrow} \qquad\qquad\qquad H_3O^+$$
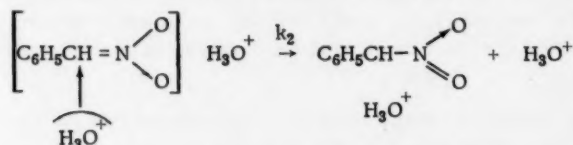
The adoption of this scheme for the reaction brought our measured velocities into agreement with all the experimental facts. However, one difficulty did arise, whose resolution would require very high experimental precision. The value of K'_N, which we calculated from $k^{H_2O}_{ND}$ and $k^{H_3O^+}_{NR}$, was very close to K_N. In practice this meant that K was small (see equation 2); and both forms of anion were present in the solution in considerable quantities. The anion $C_6H_5C^-HNO_2$ should therefore be detectable spectroscopically. In fact, in the infrared spectrum of the potassium salt, we found intense absorption bands at 1385 and 1560 cm^{-1}, which could be attributed to the symmetrical and antisymmetrical vibrations of the nitrogroup in its true form. There was also a medium intensity band at 1670 cm^{-1}, corresponding to the C = N double bond and providing evidence of the existence of the aci-anion* (see table). The data of Salyamon and Bobich [12], on the spectra of anions of the type ArN^-NO_2, confirmed the attribution of the frequencies to the true nitrogroup in compounds having a negative charge on the adjacent atom. Thus, spectroscopic confirmation was obtained of the existence in the phenylnitromethane potassium salt of the two types of anion, $C_6H_5C^-HNO_2$ and $C_6H_5CH = NOO^-$. Further spectroscopic work in this direction is proceeding.

Characteristic Frequencies, cm^{-1}

In model compounds	Dry K salt in KBr	Na salt in conc. aq. solution
In phenylnitromethane $-N \overset{O^+ \text{ sym. } 1380}{\underset{O^- \text{ antisym. } 1558}{\big\langle}}$	1385	–
	1560	1558
In aci-nitrocompounds $C = N \overset{O}{\underset{O^-}{\big\langle}}$ 1670 [11]	1670	1653

Experimental error did not allow us to determine K precisely, but polarographic measurements showed that it could not be very small. Thus, acidification of a phenylnitromethane salt should first produce a mixture of the nitro- and aci-forms, in a ratio corresponding to that of the concentrations of their ions in the salt solution and their rates of recombination. It was found experimentally that the polarographic wave height of the first formed mixture of aci- and nitro-forms was 1.5 times the wave height of the pure nitro-form. Reduction of the nitro-form should require 4 electrons, and of the aci-form 6 electrons, so that the theoretical ratio of the wave heights should also be 1.5 assuming the diffusion coefficients of both forms to be the same. This agreement showed that acidification produced mainly the aci-form, i.e. that, allowing for errors in measurement, K should not be less than 10.

Summing up the results of our kinetic investigation, we find the following picture of the tautomeric transformations of phenylnitromethane in aqueous solution, for the particular case when the base is only H_2O and the acid is H_3O^+: (See scheme on next page).

The framework of this scheme includes the fact that the aci-form is produced almost entirely when the salt is acidified with a strong acid. This is because, in the presence of a high hydrogen ion concentration, the first order velocity constant $k^{H_3O^+}_{NR}$ is greater than k_2, and this also leads to the formation of the aci-form, although $k^{H_3O^+}_{NR} > k^{H_3O^+}_{AR}$.

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*The infrared spectra were recorded by V. I. Slovetskii and V. A. Shlyapochnikov.

$$C_6H_5CH_2NO_2 + H_2O \underset{k_{NR}^{H_2O^+}}{\overset{k_{ND}^{H_2O}}{\rightleftharpoons}} C_6H_5C^-HNO_2 + H_3O^+ \qquad K'_N$$

$$k_1 \uparrow\downarrow k_2 \qquad\qquad K$$

$$K^A$$

$$C_6H_5CH=NOOH + H_2O \underset{k_{AR}^{H_2O^+}}{\overset{k_{AD}^{H_2O}}{\rightleftharpoons}} C_6H_5CHNOO^- H_3O^+$$
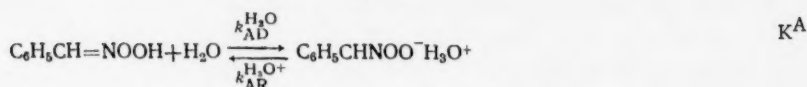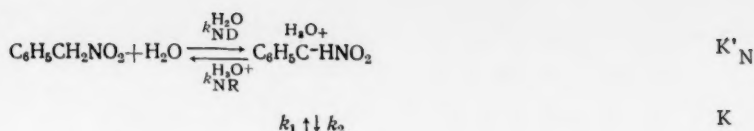
$K'_N \approx 2\cdot 10^{-7}$ mole/liter $\quad k_{ND}^{H_2O} = 8\cdot 10^{-7}$ liter/mole $\cdot$ sec $\quad k_{NR}^{H_2O^+} = 200$ liter/mole $\cdot$ sec

$K_A = 1,3\cdot 10^{-4}$ mole/liter $\quad k_{AD}^{H_2O} = 4,14\cdot 10^{-5}$ liter/mole $\cdot$ sec $\quad k_{AR}^{H_2O^+} = 18$ liter/mole $\cdot$ sec

The above results show that the dual activity of the phenylnitromethane ion can evidently be attributed to the simultaneous existence of two types of ion in solution; the iomerization of these ions proceeds slowly, and its rate in some cases determines the direction of a reaction on one side or the other. Phenylnitromethane is a typical tautomeric compound, an we therefore suggest that this phenomenon is of general importance and can be used to explain dual reactivity in other tautomeric compounds.

SUMMARY

1. A kinetic analysis of the tautomeric transformation of phenylnitromethane confirms that there are two forms of anion, namely the aci-anion and the nitro-anion.

2. It has been established for the first time, for the case of phenylnitromethane, that dissociation of the aci-form is the stage determining the rate of isomerization of aci- to nitro-form in an acid medium.

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INVESTIGATIONS IN THE FIELD OF THE CHEMICAL TRANSFORMATIONS OF UNSATURATED AND HIGH-MOLECULAR COMPOUNDS

15. COPOLYMERIZATION OF SOME VINYL ETHERS WITH METHACRYLIC ACID

M. F. Shostakovskii and A. M. Khomutov

N. D. Zelinski Institute of Organic Chemistry of the Academy of Sciences, USSR

In previous communications it has been shown that when vinyl alkyl (aryl) ethers copolymerize with methacrylic acid, competing reactions are observed: polymerization and the formation of monomolecular compounds [1,2]. In order to elucidate the behavior of other representatives of the vinyl ethers on copolymerization with methacrylic acid, we have studied the divinyl ethers as an example. In the present communication we discuss the copolymerization of methacrylic acid with the divinyl ethers of the following structure: $CH_2=CHOCH=CH_2$ (I) and $CH_2=CHOCH_2CH_2OCH=CH_2$ (II).

We employed these ethers because of the following properties. Ether (I) is more prone to reaction by a radical mechanism [3]; it is easily polymerized on storage, on heating, and also in the presence of initiators (benzoyl peroxide and azoisobutyric acid dinitrile), and the conditions for its polymerization under the influence of ionic catalysts had not yet been demonstrated; ether (II) does not polymerize under the influence of the initiators mentioned and is easily polymerized in the presence of ferric chloride [4]. By analogy with the vinyl alkyl ethers it would be expected that the divinyl ethers would enter into a copolymerization reaction with methacrylic acid and acylals of the following structure would be formed:

$$2CH_2=C(CH_3)+CH_2=CHOCH=CH_2$$
$$|$$
$$COOH$$

$$CH_2=C(CH_3) \qquad (CH_3)C=CH_2$$
$$| \qquad\qquad\qquad /$$
$$COOCHOCHOOC \qquad\qquad (III)$$
$$| \qquad |$$
$$CH_3 \qquad CH_3$$

$$CH_2=C(CH_3) \qquad\qquad CH_2=C(CH_3)$$
$$| \qquad\qquad\qquad\qquad |$$
$$COOCHOCH_2CH_2OCHOOC \qquad\qquad (IV)$$
$$| \qquad\qquad |$$
$$CH_3 \qquad\qquad CH_3$$
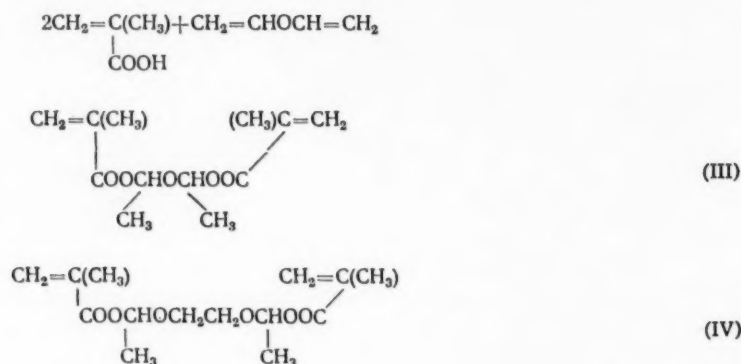
The first series of experiments on the copolymerization of divinyl ether (I) with methacrylic acid was carried out in the presence of benzoyl peroxide and the following relationship was established: when the divinyl ether in the reaction medium is increased, the yields of the copolymer decrease, but the number of units of the ether in the copolymer increases (Fig. 1). From Fig. 1 it is seen that the composition curve for the copolymer is

reminiscent of that for the copolymerization $r_1 > 1$ and $r_2 < 1$ [5]. This similarity in the curves might lead to the conviction that in this case also constants of copolymerization can be calculated; however, acylals were found in the composition of the copolymer, i.e., the reaction was accompanied by consumption of the copolymer not only in increasing the polymer chain, but also in the formation of the acylals (III). It is well known that for such competitive reactions the modern theory of copolymerization excludes the possibility of calculation of the constants (r_1 and r_2) [6].

The second series of experiments on the copolymerization of divinyl ether (I) with methacrylic acid was carried out in the presence of azoisobutyric acid dinitrile. In Fig. 1 the relationship between the yields, composition, and molar concentration of the starting monomers is shown. In this case, when the concentration of divinyl ether in the reaction medium increased, the yields of copolymers at first fell and then began to increase; the number of units of divinyl ether in the copolymer increased.
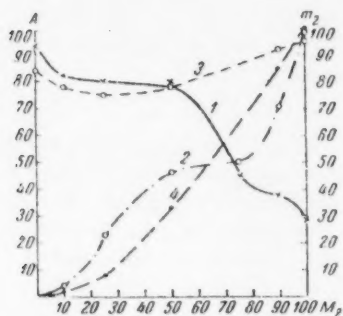
Fig. 1. Copolymers of methacrylic acid and divinyl ether. A) yields in percent; m_2-molar content of divinyl ether units in the copolymer in %; M_2-initial concentration of monomer of divinyl ether in mole-%; 1 and 2- for benzoyl peroxide; 3 and 4- for azoisobutyric acid dinitrile.
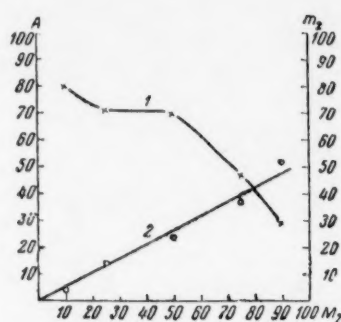
Fig. 2. Yields and composition of copolymers of divinyl ether of ethylene glycol and methacrylic acid. A) yields in % (curve 1); M_2-initial concentration of monomeric divinyl ether of ethylene glycol in mole-%; m_2-molar content of units of divinyl ether of ethylene glycol in copolymer in % (curve 2).

In the composition of the copolymers, acylals (III) were found which were formed as a result of the competing reactions that were observed. In comparing the copolymerization of divinyl ether and methacrylic acid in the presence of benzoyl peroxide and azoisobutyric acid dinitrile, it must be noted that the nature of the initiator significantly affects the yields and composition of the copolymers (Fig. 1). In general for both cases it appears that the copolymers obtained have a trimeric structure and the number of units of divinyl ether (I) in their make-up is greater than 50 mole-%; in this respect they differ from the vinyl alkyl ethers, which form linear copolymers with methacrylic acid and the number of units of which in the composition of these copolymers does not exceed 50 mole-%. If the vinyl alkyl ethers contain a functional group with a labile hydrogen in the alkoxyl radical, then competing reactions are observed which lead to the formation of divinyl compounds that may result in the production of cross-linked copolymers. In the case of copolymerization of divinyl ether (I) with methacrylic acid, the cross-linking may be represented by the following diagram: (See scheme on next page).

Let us proceed to a description of the copolymerization reaction with the divinyl ether of ethylene glycol (II). The copolymerization of this ether with methacrylic acid proceeds somewhat differently than that of divinyl ether (I) and accordingly approaches the reactions of the vinyl alkyl ethers. The copolymers containing more than 15% of units of the divinyl ether of ethylene glycol have a "trimeric structure", but their content in the copolymers does not exceed

$$\cdots-CH_2-CH\cdots-CH_2-C(CH_3)-CH_2-CH-\cdots$$

structure (V) and (VI) chemical diagrams:

```
··—CH₂—CH··—CH₂—C(CH₃)—CH₂—CH—··
        |              |            |
        O            COOH           O          CH₃
··—CH—CH₂—CH—CH₂—··  ··—CH—CH₂—C—CH₂—··          (V)
        |                          |
        O                        COOH
··—CH—CH₂—··
```

```
—CH₂—C(CH₃)—···        —C(CH₃)—CH₂—···
        |                   |
      COOCH—O—CHOOC                                (VI)
        |        |
       CH₃      CH₃
```
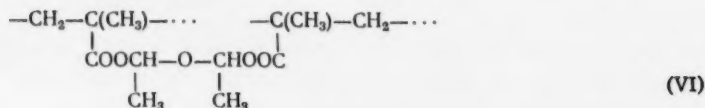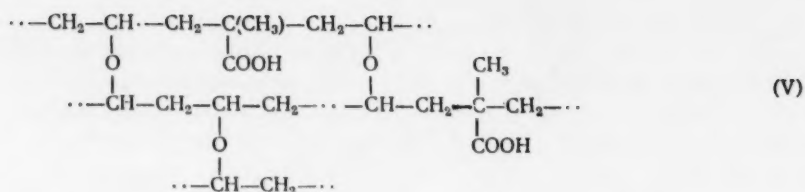
50 mole-%. The relationship established by us previously [7] is observed between the composition of the copolymers, the yields, and the concentration of the starting monomers with an increase in the amount of divinyl ether of ethylene glycol in the reaction medium the yields of copolymers decrease, but the number of units in them increases. This relationship is shown graphically in Figure 2 and is expressed by a straight line. The magnitude of tan α was calculated from the data on the number of units of divinyl ether of ethylene glycol in the copolymer (m_2) and the starting concentration of this monomer in the reaction medium (M_2^0); the values of tan α are given in Table 1.

TABLE 1

Value of tan α for Initial Concentration M_2^0

M_2^0 in mole-%	m_2 in mole-%	tan α
10	5,0	0,5
25	14,3	0,54
50	24,0	0,48
75	37,8	0,5
90	52,1	0,57

In order to establish the composition of the copolymers, they were hydrolyzed, the acetaldehyde content was determined, and the amount of acylals was calculated. The acylal content in these copolymers with divinyl ether, which may explain the smaller tendency of the divinyl ether of ethylene glycol to reactions by a radical mechanism.

EXPERIMENTAL

The starting monomers used for the investigations were freshly distilled methylacrylic acid with b.p. 160°, n_D^{20} 1.4312, d_4^{20} 1.015; divinyl ether with b.p. 28° (745 mm), n_D^{20} 1.3982, d_4^{20} 0.7734; divinyl ether of ethylene glycol with b.p. 126-127°, n_D^{20} 1.4438, d_4^{20} 0.9145.

The copolymerization reaction was carried out at $60 \pm 1°$ continuously. The duration of the reaction was 100 hours. After the polymerization was ended, the ampoules were cooled in a mixture of acetone and solid carbon dioxide. The copolymerization was studied with various molar ratios of the starting monomers. The experimental data are reported below.

Copolymerization of divinyl ether with methacrylic acid in the presence of benzoyl peroxide. Two and three tenths grams of divinyl ether and 2.7 g of methacrylic acid were placed in ampoules with 0.01 g of benzoyl peroxide. The ampoules were sealed, shaken, and heated. The copolymers formed were insoluble in water and organic solvents and did not melt when heated; they were ground and methanol was added to extract the monomers; the extraction was terminated when the solution gave a negative test for a double bond. Then the copolymers were dried to constant weight. Since there was a large difference between parallel determinations when the carboxyl groups of the copolymer were titrated with alkali, the composition of the copolymers was calculated from the data from elementary analysis. The methacrylic acid in the methanol with which the copolymers were extracted was determined by titration with alkali. The amount of unreacted methacrylic acid found was 0.05 g, i.e., the copolymer contained 2.65 g of methacrylic acid. The yield of copolymer was 3.89 g. From this it is possible to calculate the content of methacrylic acid units in the copolymer as 68%, and that of divinyl ether as 32%. The data from elementary analysis permit calculation of the composition of the copolymer: methacrylic acid units 65.8%, divinyl ether 34.2%. We may conclude that the methacrylic acid was completely extracted from the trimeric copolymer. At the same time it was possible to verify the data from the elementary analysis. The experimental data on the copolymerization of methacrylic acid and divinyl ether in other molar ratios of the starting monomers are given in Table 2. The results of the determination of acylals in the composition of the copolymers also are given in this table.

TABLE 2

Copolymerization of Methacrylic Acid (III) and Divinyl Ether (I) in the Presence of Benzoyl Peroxide

Amount of monomers in g		Yield of polymers in g	C determined in copolymer in %	Composition of copolymers in wt-%		Unreacted methacrylic acid in g	Acylal content of copolymer in %
(III)	(I)			(III)	(I)		
5,0	—	4,59	55,8	100	—		
4,59	0,41	4,35	56,24	96,6	3,4	0,44	
3,9	1,1	4,25	57,9	83,6	16,5	0,27	1,2
2,7	2,3	3,89	60,18	65,8	34,2	0,05	1,1
1,45	3,55	2,21	61,48	55,7	44,3	0,02	1,4
0,6	4,4	1,68	64,97	28,3	71,7	0,01	
—	5,0	1,48	68,6	—	100	—	

TABLE 3

Copolymerization of Methacrylic Acid (III) and Divinyl Ether (I) in the Presence of Azo-isobutyric Acid Dinitrile

Amount of monomers in g		Yield of copolymers in g	C determined in copolymers in %	Composition of copolymers in wt-%		Unreacted methacrylic acid in g	Acylal content of copolymer in %
(III)	(I)			(III)	(I)		
5,0	—	4,59	55,8	100			
4,59	0,41	4,11	56,0	98,4	1,6	—	
3,9	1,1	3,91	56,6	93,7	6,3·	0,89	3,25
2,7	2,3	3,84	59,45	71,5	28,5	0,08	3,0
1,45	3,55	4,0	64,12	35,2	64,8	0,021	4,3
0,6	4,4	4,65	66,45	16,8	83,2	0,016	
—	5,0	4,72	68,6	—	100		

TABLE 4

Copolymerization of Divinyl Ether of Ethylene Glycol (II) and Methacrylic Acid (III) in the Presence of Azoisobutyric Acid Dinitrile

Amount of monomers in g		Yield of copolymers in g	Units of methacrylic acid determined in copolymer in %	Composition of copolymers in wt-%		Unreacted methacrylic acid in g	Acylal content of copolymer in %
(III)	(II)			(III)	(II)		
5	—	4,59	99,2	100	—	—	—
4,35	0,65	4,0	93,44	93,44	6,59	—	—
3,47	1,53	3,56	81,1	81,1	18,9	0,89	
2,15	2,85	3,0	71,27	71,27	28,73	0,08	10,15
1,0	4,0	1,9	55,4	55,4	44,6	0,021	18,7
0,38	4,62	0,9	41,0	41,0	59,0	0,016	—
—	5		Polymer not isolated				

Copolymerization of divinyl ether and methacrylic acid in the presence of azoisobutyric acid dinitrile. The copolymerization of equimolar amounts of divinyl ether (2.3 g) and methacrylic acid (2.7 g) with, 0.01 g of azoisobutyric acid dinitrile, the separation of the copolymer, and the analyses were carried out as described above. The methacrylic acid determined in the methanol solution (after extraction of the copolymer) was 0.04 g, i.e., the copolymer contained 2.66 g of methacrylic acid units. Knowing the yield of copolymer (3.84 g), we calculated the composition of the copolymer: methacrylic acid units 70%, divinyl ether 30%. According to the data from the elementary analysis the calculated composition of the copolymer was: methacrylic acid units 71.5%, divinyl ether 28.5%. The quantitative composition found for the copolymer is close. Divinyl ether and methacrylic acid were compolymerized in various molar ratios. After hydrolysis of the copolymers, acetaldehyde was determined and the acylals were quantitatively calculated. The data are given in Table 3.

Copolymerization of divinyl ether of ethylene glycol with methaacrylic acid in the presence of azoisobutyric acid dinitrile. Equimolar amounts of the divinyl ether of ethylene glycol (2.85 g) and methacrylic acid (2.15 g) were copolymerized, with 0.01 g of the azoisobutyric acid dinitrile. The composition of the copolymers was determined by titration of the carboxyl groups with alkali. The data from parallel determinations were satisfactory. The methacrylic acid determined in the methanol solution (after extraction of the copolymer) was 0.08 g. The yield of copolymer was 3 g. From this information its composition was calculated: 69% of methacrylic acid units and 31% of ethylene glycol divinyl ether units. The carboxyl groups were determined in the copolymer by titration and its composition was calculated: 71.27% of methacrylic acid units and 28.73% of ethylene glycol divinyl ether units. There was 10.15% of acylals in the copolymer. The experimental data on the copolymerization of the monomers mentioned, at other concentrations, are given in Table 4.

The solubility of the copolymers synthesized was determined. Copolymers containing 6.56 mole-% of divinyl ether of ethylene glycol dissolved in methanol. All the rest of the copolymers were insoluble in water and organic solvents and did not melt.

SUMMARY

1. The copolymerization of divinyl ether (I) and of the divinyl ether of ethylene glycol (II) with methacrylic acid in the presence of benzoyl peroxide and azoisobutyric acid dinitrile has been studied.

2. The copolymers of divinyl ether (I) and of the divinyl ether of ethylene glycol (II) with methacrylic acid have a trimeric structure; the copolymers containing up to 6.56 mole-% of ethylene glycol divinyl ether units are an exception.

3. Under the influence of various iniators the copolymerization of divinyl ether (I) and of the divinyl ether of ethylene glycol (II) with methacrylic acid is accompanied by competing reactions.

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KINETICS AND CHEMICAL NATURE OF THE POLYCONDENSATION
OF ESTERS OF α-AMINO ACIDS AND PEPTIDES

II. JOINT POLYCONDENSATION OF ESTERS AND N-CARBOXYLIC ANHYDRIDES
OF D,L-ALANINE AND GLYCINE

K. T. Poroshin, Yu. I. Khurgin, and N. I. Prokhorova

N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences USSR,

We have previously studied the reaction of the ethyl ester and the N-carboxylic anhydride of glycine [1,2] and D, L-alanine in solution [3] and also without a solvent (en masse). With small relative molar concentrations of the anhydride and ester (A/E < 1) and in the absence of a solvent, the reaction proceeds mainly by the mechanism characteristic of the polycondensation of esters of α-amino acids in the presence of carbon dioxide, since the carbon dioxide liberated by the decomposition of the anhydride of the N-carboxy-α-amino acid combines with the ester of the α-amino acid in the form of the so-called symmetrical carbamate $R'OOC.NH_3^+ . ^-OOC.CHR.COOR'$.

According to the mechanism previously proposed for the polycondensation of the esters of α-amino acids, the growth of the peptide chains proceeds by way of the reaction of the symmetrical carbamate with the amino—group of the peptide or the amino acid [4]. If the reaction of the ester and the anhydride of the amino acid takes place in solution, however, the role of the carbamates in the formation and particularly in the growth of the peptide chains is comparatively small. When the ethyl ester and the N-carboxylic anhydride of glycine react, all of the anhydride breaks down comparatively quickly at the beginning of the reaction with the formation of short peptide chains ($n_1 = 4-5$) and diketopiperazine, while in the later stages the composition of the reaction products changes comparatively slowly.

In the joint polycondensation of the ester and the anhydride of D, L-alanine comparatively long peptide chains are formed slowly, probably mainly as a result of the breakdown of the anhydride. Diketopiperazine is formed mainly by the carbamate mechanism. The data obtained previously did not permit a demonstration of whether the symmetrical carbamates take part in the formation of the peptide chains. To resolve this problem we studied the kinetics of the change in composition of the products of joint polycondensation of the esters and the N-carboxylic anhydrides of different amino acids. In connection with the fact that a method for the determination of the free esters of amino acids had been developed, we repeated the experiments on the study of the joint polycondensation of the derivatives of glycine and alanine. Here we were able to compare the rate of reaction of the ethyl esters and the anhydrides of glycine and alanine. A study of the composition of the peptides showed that the role of the carbamate mechanism in the joint polycondensation had no practical significance in the formation of the peptides.

EXPERIMENTAL

Reaction of the anhydride of N-carboxy-D, L-alanine with the ethyl ester of glycine. The reaction of the anhydride of N-carboxy-D,L-alanine with the ethyl ester of glycine in the ratio A/E = 0.5* went very slowly. In

---

*A/E is the initial relative concentration of the N-carboxylic anhydride and the ester of the α-amino acid.

120 hours only 30% of the glycine ester reacted (Fig. 1), after 120 hours the yield of reaction products reached 25% and practically did not increase further (Fig. 2). The concentration of diketopiperazine in the solid phase remained constant. The data on the yield of diketopiperazine (in moles) are given in Figures 3 and 4. The peptide fraction, constituting approximately 80% of the solid phase, consisted of comparatively long peptides. The average degree of polymerization(n_1)of the peptide fraction of the reaction products at 50 hours reached the value $n_1 = 22$; later, when the process slowed down, the length of the peptides increased slowly; the average degree of polycondensation at 120 hours reached the value $n_1 = 30$. Chromatographic investigation showed that the reaction products
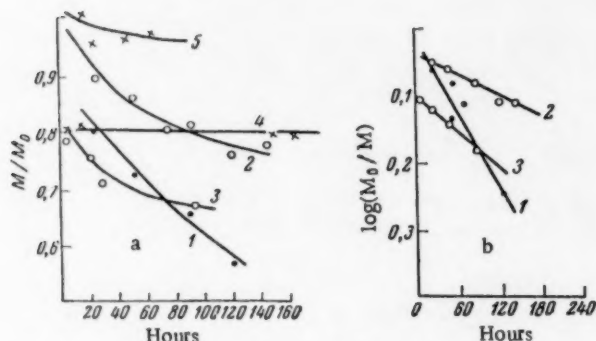

Fig. 1a. Kinetics of combination of the ester of the amino acid in the course of polycondensation: 1) A/E = 0.5 (an-hydride of N-carboxy-D,L-alanine + ethyl ester of glycine); 2) A/E = 0.5 (anhydride of N-carboxy-glycine + ethyl ester of alanine); 3) A/E = 0.08 (anhydride of N-carboxy-D,L-alanine + ethyl ester of glycine); 4) A/E = 0.5 (anhydride of N-carboxy-D, L-alanine + ethyl ester of alanine); 5) A/E = 0.5 (anhydride of N-carboxyglycine + ethyl ester of glycine); M/M is the concentration of the free ester of the amino acid.

Fig 1b. The same data on semilogarithmic coordinates.

Fig. 2. Yield of the solid phase (s.p.) (% of starting materials): 1) A/E = 0.5 (anhydride of N-carboxy-D,L-alanine + ethyl ester of glycine); 2) A/E = 0.5 (anhydride of N-carboxyglycine + ethyl ester of alanine); 3) A/E = 0.08 (anhydride of N-carboxy-D,L-alanine + ethyl ester of glycine).

were formed mainly by the anhydride of N-carboxy-D,L-alanine. Determination of the N-terminal amino acids through the dinitrophenyl derivatives [5] showed the presence only of alanine. Glycine peptides and diketopiperazine were found in insignificant amounts.

The reaction of the ethyl ester of glycine with the anhydride of N-carboxy-D,L-alanine at a ratio A/E = 0.08 went considerably slower than in the case of A/E = 0.5. When A/E = 0.08, in 100 hours only 20% of the initial amount of the glycine ester reacted (Fig. 1). The accumulation of products proceeded extremely slowly; in 120 hours the yield of the solid phase reached only 3.5% relative to the starting materials; this value did not change further (Fig. 2), since the reaction practically ceased.

Reaction of the ethyl ester of D,L-alanine with the anhydride of N-carboxyglycine. The reaction of the ethyl ester of D,L-alanine in the presence of the anhydride of N-carboxyglycine in the ratio A/E = 0.5 went somewhat more slowly than in the experiments described above, but in this case in the first stage of the reaction the products of the polycondensation accumulated more rapidly, although the yield of the solid phase at the end of the reaction was somewhat less. In 3 hours the yield of the solid phase was 12.5% relative to the starting materials, and in 25 hours the yield of solid phase increased only to 20% and showed almost no further change (Fig. 2). In 3 hours only 20% of the starting amount of the alanine ester reacted, after which the rate of consumption sharply dropped. The average degree of polymerization of the peptide fraction at 25 hours from the start of the reaction reached the value $n_1 = 4$ (3.88) and remained practically unchanged (120 hours, $n_1 = 391$). By differential titration it was determined that in the main the composition of the polycondensation products, starting with 25 hours, from the beginning of the reaction, did not change, since under these conditions the rates of formation of the reaction products- the tri and tetrapeptide fractions and diketopiperazine-were approximately the same. In the determination of the N-terminal amino acids by the dinitrophenyl method, only glycine was found.
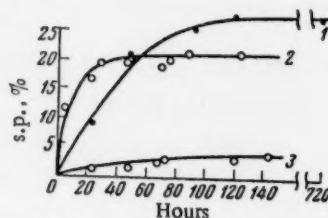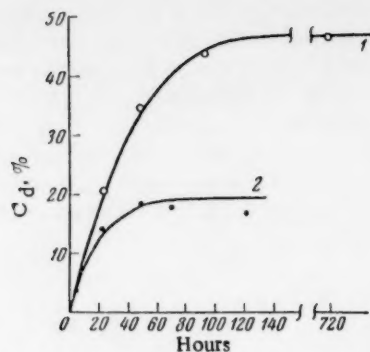
Fig. 3. Diketopiperazine content (in % of the solid phase): 1) A/E = 0.5 (anhydride of N-carboxy-D,L-alanine + ethyl ester of glycine); 2) A/E = 0.5 (anhydride of N-carboxyglycine + ethyl ester of alanine).
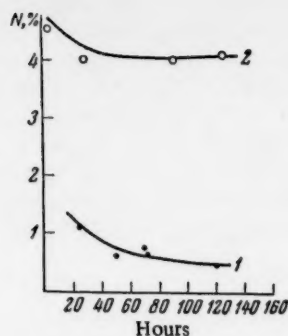
Fig. 4. Concentration of amino nitrogen in the solid phase: 1) A/E = 0.5 (anhydride of N-carboxy-D,L-alanine + ethyl ester of glycine); 2) A/E = 0.5 (anhydride of N-carboxyglycine + ethyl ester of alanine).

The reaction of the ethyl ester of D,L-alanine in the presence of a small amount of the anhydride of N-carboxyglycine at A/E = 0.08 goes considerably more slowly than in all the other cases investigated by us. In a period of more than 150 hours we were not able to find any noticeable decrease in the alanine ester content of the reaction products formed.

In connection with the refinement in the method of determining the unreacted ester of the amino acid we also again studied the reaction of the ethyl esters of glycine and D,L-alanine with the corresponding N-carboxylic anhydrides. The data on the consumption of the esters of the amino acids are given in Fig. 1. The yield of the solid phase and the values of the average degree of polymerization of the reaction products are in agreement with the data obtained previously.

DISCUSSION OF EXPERIMENTAL RESULTS

The data obtained on the kinetics of the change in composition of the products of the reaction of the esters and the N-carboxylic anhydrides of glycine and D,L-alanine are given in the table. From these data it is seen that

Ethyl ester of amino acid	Glycine		Glycine		Alanine		Alanine	
anhydride of N-carboxylic acid	glycine		alanine		alanine		glycine	
A/E	0,5	0,08	0,5	0,08	0,5	0,08	0,5	0,08
Rate constant of expenditure of ester of amino acid (k in sec^{-1})	$<10^{-7}$	$<10^{-7}$	$1{,}31 \cdot 10^{-6}$	$1{,}95 \cdot 10^{-7}$	$<10^{-7}$	$<10^{-7}$	$4{,}02 \cdot 10^{-7}$	$<10^{-7}$
Amount of ester of amino acid bound in the initial stage (in %)	~20	—	0	0	0	0	~20	~10
Yield of solid phase* (in % of starting materials)	~20	6	20	2	11	5	26	3,5
Diketopiperazine content (in % of solid phase)*	11	11	50	—	50	58	20	—
Average degree of polymerization of reaction products*	~5	4,5	4	—	4,5	12	22	—

* In the final stage of the reaction.

the N-terminal amino acids are included in the composition of the peptides by way of the addition of the N-carboxylic anhydrides. The analysis of the amino acid composition of the peptides and the N-terminal amino-acids indicates that the esters of the amino acids participate only in the formation of new chains, i.e., the esters of the amino acids are initiators of the polycondensation of the anhydrides of the N-carboxyamino acids. In this connection the data on the reaction of the ethyl ester of glycine with the anhydride of N-carboxy-D,L-alanine are of the greatest interest, since in this case comparatively short peptides are formed. The complete absence of DNP-glycine is associated with the fact that the symmetrical carbamates take practically no part in the formation of the chains when the reaction takes place in a comparatively dilute solution (5%). In this case the formation of the peptides takes place in the following manner:

$$NH_2 \cdot CHR \cdot COOR' + \begin{array}{c} NH-CO \\ | \\ RCH-CO \end{array} \Big\rangle CO \longrightarrow NH_2 \cdot CHR \cdot CO \ldots NH \cdot CHR \cdot CONHCHR \cdot COOR'.$$
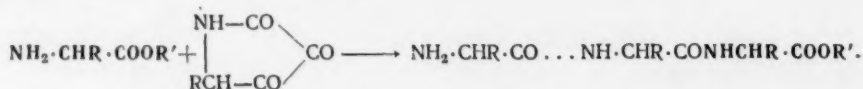
The peptides formed by polycondensation in solution differ in their amino acid composition only in the C-terminal amino acid. Chromatographic analysis shows that the diketopiperazine fraction consists mainly of alanyl-glycine diketopiperazine and contains only a small amount of diketopiperazine formed from two molecules of the ester of the α-amino acid. In this connection it is important to note that the consumption of ester of the amino acid agrees rather exactly with the total molar yield of peptides and diketopiperazine. This is in accord with the conclusion that each molecule of peptide and diketopiperazine contains in its composition only one amino acid residue entering into the makeup of the ester.

In the presence of an excess of amine, the anhydrides of the N-carboxy-α-amino acids form the corresponding amides of the amino acids. When an excess of the esters of the α-amino acids react, therefore, with the anhydride of N-carboxy-α-amino acids ($A/E = 0.5$ or 0.08) it would be expected that mainly the corresponding ester of the dipeptide would be formed, which would be partially converted to diketopiperazine. Actually the products of the reaction of the anhydride of N-carboxy-D,L-alanine with the ethyl esters of glycine or D,L-alanine contain up to 50% of diketopiperazine. In the very earliest stages of the reaction, however, a considerable amount of peptides are formed which contain three and more amino acid residues. In the joint polycondensation of the anhydride of N-carboxyglycine with the ester of D,L-alanine, peptides are formed containing 20 and more amino acid residues. The formation of comparatively long peptides when an excess of the ester of an amino acid reacts with the anhydrides of N-carboxylic amino acids may be associated with the increase in the reactivity of the amino group of the peptides in comparison with the amino group of the amino acid. This phenomenon recalls the autocatalytic nature of the polycondensation of the esters of the α-amino acids in the presence of carbon dioxide, which was discovered by us.

The relative yield of diketopiperazine and peptides, the rate of reaction, and a number of other characteristics of the reaction depend greatly on the choice of ester and N-carboxylic anhydride of the amino acid. As a result of the greater reactivity of the anhydride of N-carboxyglycine (in comparison with the anhydride of alanine), its reaction with the esters of the amino acids in the initial stages is accompanied by the combination of a considerable amount of the ester of the amino acid. In the polycondensation of the anhydride of N-carboxy-D,L-alanine the first rapid stage is not observed. The choice of anhydride also determines the yield of diketopiperazine. The products of polycondensation of N-carboxylic anhydrides of glycine and alanine contain 10-20 and 50%, respectively, of diketopiperazine.

In the joint polycondensation of the esters and the N-carboxylic anhydrides of the different amino acids, the yield of diketopiperazine is in conformance with the relative rates of cyclization of the ethyl esters of alanyl-glycine and glycylalanine [6]. The average degree of polymerization of the polycondensation products is associated with the relative rates of conversion of the ester of the dipeptide to the diketopiperazine and to longer peptide.

The polycondensation of the esters of α-amino acids in the presence of carbon dioxide, symmetrical carbamate, and the anhydrides of N-carboxyamino acids in the presence of amines, including the esters of the amino acids, proceed through the same stages-formation of unsymmetrical carbamates. Analysis of the kinetics of the polycondensation, taking into account the formation of the unsymmetrical carbamates, shows that the stage determining the rate of reaction may be the formation of the carbamate of the ester of the dipeptide $R'OOC \cdot CHR \cdot NH_3^+ \cdot OOC \cdot NH \cdot CHR \cdot CO \cdot NH \cdot CHR \cdot COOR'$ and the breakdown of the unsymmetrical carbamates. In the polycondensa-

tion of the anhydride of N-carboxyglycine the stage determining the rate is the breakdown of the unsymmetrical carbamates, and in the polycondensation of the anhydride of N-carboxy-D,L-alanine it is the formation of the unsymmetrical carbamate of the ester of the dipeptide. This conclusion is in agreement with the observations of the differences in the rates of polycondensation of the N-carboxylic anhydrides of glycine and alanine initiated by amines.

SUMMARY

1. The reaction of the N-carboxylic anhydrides and ethyl esters of glycine and D,L-alanine in solution has been studied.

2. The composition of the polycondensation products has been studied. The role of the esters and the N-carboxylic anhydrides in the formation of peptide chains has been established.

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ADDITION OF HYDROGEN HALIDES TO FLUORO OLEFINS

I. L. Knunyants, V. V. Shokina, and N. D. Kuleshova

Institute of Heteroorganic Compounds, Academy of Sciences, USSR

Addition of nucleophilic reagents to fluoro olefins is at present being widely investigated. As would be expected, electrophilic reagents, as a result of the marked electron deficiency of the π-bond in fluoro olefins, combine with fluoro olefins with difficulty, and these reactions can be carried out only at elevated temperatures, using catalysts. Rate of addition of HF to fluoro olefins decreases with increase in number of halogen atoms, especially of fluorine, in the olefin [1-3]. The literature existing at present regarding addition of hydrogen halides to fluoro olefins deals mainly with tetrafluoroethylene and several fluorochloro olefins. Addition of HF [4] and HBr to perfluoropropylene and several other fluorochloro olefins has been carried out [5-7]. For perfluoroisobutylene, reactions of a similar type are still unknown.

As shown in the present investigation, hydrogen halides evidently combine with perfluoroisobutylene somewhat more readily than with perfluoropropylene. Thus, HF combines with perfluoroisobutylene under pressure on heating to 200°C; the reaction is completed in 24 hours; heating for not less than 100 hours is necessary for perfluoropropylene under the same conditions. Addition of HCl and HBr was achieved in the vapor phase without resorting to pressure, over a catalyst (a mixture of carbon and $CaSO_4$), addition to perfluoroisobutylene occurring at 200°; elevation of temperatures to 230° is necessary for perfluoropropylene. Order of addition corresponds to the distribution of electron density in the olefin molecule, that is, hydrogen is added to the carbon bearing a trifluoromethyl group

$$CF_3-CF{=}CF_2 + HX \longrightarrow CF_3-CFH-CF_2X$$

$$\begin{array}{c}CF_3\\CF_3\end{array}{\Big>}C{=}CF_3 + HX \longrightarrow \begin{array}{c}CF_3\\CF_3\end{array}{\Big>}CH-CF_2X,$$
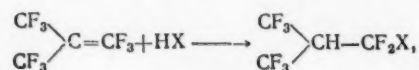
where X = F, Cl, Br. This has also been confirmed by comparison of nuclear magnetic resonance spectra of F^{19} in the compounds obtained with the spectra of compounds containing known groupings of this type. Values for the relative chemical displacement for the products are shown in the table.

All attempts at adding HI to perfluoropropylene and perfluoroisobutylene were unsuccessful. The monohydromonohaloperfluoroisobutanes obtained were stable toward acidic and acidifying reagents, for instance, toward prolonged boiling with nitric acid of specific gravity 1.52. By reacting with bases ($NaHCO_3$, pyridine, aniline), the hydrogen halide was readily split off from them again. Similar propane derivatives were relatively more stable.

EXPERIMENTAL

Addition of HF. Into a 200 ml steel test tube were placed 3 g of catalyst* and 100 g of 30% hydrofluoric acid (a 10-fold excess). The test tube was cooled to -60°, 30 g of perfluoropropylene or perfluoroisobutylene added,

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*Activated carbon and $CaSO_4$ were mixed in the proportion 3:1 and heated in vacuo for 2 hours at 200°.

Initial olefin	Hal	Reaction temp. in °C/time in hours	Product	% Yield olefin used in reaction	b.p. °C	d_0^0	n_D^{20}	Found in % C	H	F	Calculated in % C	H	F	$\delta = \dfrac{f_{sample} - f_{ref}}{f_{ref}} \cdot 10^5$ *
$CF_3-CF=CF_2$	HF	200/100	$CF_3CFH-CF_3$	80	−17			21,14	0,60	78,30	21,17	0,59	78,23	$(CF_3)_2$—6,8 CFH—19,8
"	HCl	230	$CF_3CFH-CF_2Cl$	60	16	1,519		18,67	0,47	62,51	19,03	0,53	61,12	CF_3—6,6 CF_2Cl—5,7 CFH—18,8
"	HBr	230	$CF_3CFH-CF_2Br$	50	36									CF_3—6,5 CF_2Br—5,1 CFH—18,1
"			$CF_3CFBr-CF_2Br$	10	71									
$\begin{smallmatrix}CF_3\\CF_3\end{smallmatrix}\!>\!C=CF_2$	HF	200/24	$(CF_3)_2CH-CF_3$	75	11			21,60	0,53	77,76	21,23	0,46	77,71	CF_3—6,3 $(CF_3)_2$—6,9
"	HCl	200	$(CF_3)_2CH-CF_2Cl$	45	43	1,591	1,298	20,33	0,29	64,12	20,34	0,42	64,41	$(CF_3)_2$—5,3 CF_2Cl 4,3
"	HBr	200	$(CF_3)_2CH-CF_2Br$	50	56	1,872	1,318	17,23	0,39	54,15	17,10	0,35	54,09	$(CF_3)_2$—5,5 CF_2Br—3,8

* Nuclear magnetic resonance spectra were taken by Yu. S. Konstantinov of the Chair of Radio Technique of the Faculty of Physics, Moscow State University. CF_2Cl_2 was taken as the reference sample.

and the mixture heated to 200°. For perfluoroisobutylene 24 hours' heating was sufficient, for perfluoropropylene, not less than 100 hours' heating was necessary. In the reaction with isobutylene anhydrous hydrogen fluoride was necessary instead of hydrofluoric acid; with propylene the reaction proceeds only in the presence of water. To absorb excess HF the gaseous reaction products were passed through a copper tube filled with sodium fluoride, dried by passing through a column of $CaCl_2$, condensed, and distilled on a Podbel'nyak column. In the reaction with perfluoroisobutylene, in view of the very slight difference in the boiling points of perfluoroisobutylene and monohydroperfluoroisobutane, the reaction gases were passed into alcohol to extract unreacted perfluoroisobutylene. The monohydroperfluoroisobutane was then dissolved in alcohol and distilled off from the alcohol on a Podbel'nyak column. Yields and constants of the products obtained are given in the table.

Addition of HCl and HBr. A mixture of perfluoro olefin (propylene or isobutylene) and hydrogen halide (HCl or HBr) was passed through a glass tube of length 500 mm and diameter 30 mm, filled with catalyst (carbon and $CaSO_4$). The tube was heated in an oven. Oven temperature was held at 200° in the reaction with isobutylene and at 230° in the reaction with propylene. Reaction products were carefully washed free of excess hydrogen halide with water, dried, and distilled on a Podbel'nyak column. Yield and constants of the products are given in the table.

On reacting with bases, the monohydromonohaloperfluoroalkanes obtained readily split off the hydrogen halide again.

SUMMARY

Addition of hydrogen halides to perfluoropropylene and perfluoroisobutylene was accomplished and a series of compounds prepared.

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PREPARATION OF THE β-AMINOETHYL ETHER OF DIMETHYLETHYNYLCARBINOL

G. A. Schwechheimer

N. D. Zelinskii Organic Chemistry Institute, Academy of Sciences, USSR

To prepare the β-aminoethyl ether of dimethylethynylcarbinol, which could prove interesting from the point view of physiological activity, the β-cyanoethyl ether of dimethylethylcarbinol was chosen as the starting point. On alcoholysis the latter is readily converted in high yield into the β-carbomethoxyethyl ether (I) [1]

(I)
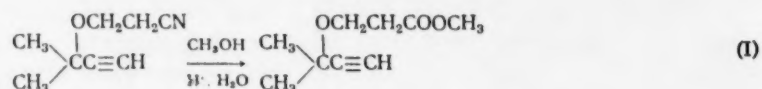
On heating the β-carbomethyoxyethyl ether of dimethylethylcarbinol (I) with hydrazine hydrate in alcohol, the corresponding hydrazide (II) was obtained as a viscous, colorless oil. Without purifying, the latter was treated with nitrous acid, and, without isolation, the azide thus formed (III) was reacted with ethyl alcohol, this resulting in the formation of the corresponding urethan (IV) as a viscous oil.

Urethan (IV), on boiling with a methanol solution of barium hydroxide or on heating with calcium oxide in the presence of water, was converted into the β-aminoethyl ether of dimethylethynylcarbinol (V).
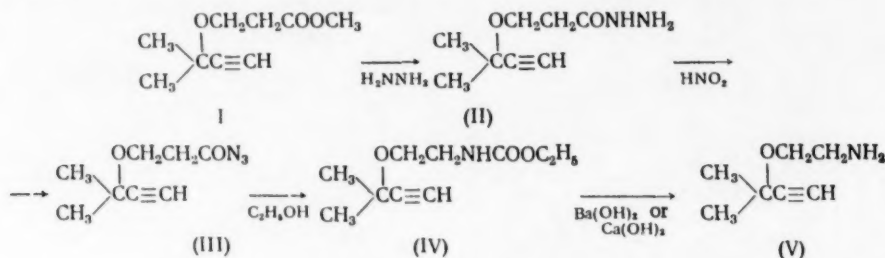
Spectroscopic data confirmed the presence of an amino group and a triple bond in the product.

EXPERIMENTAL

The β-cyanoethyl ether of dimethylethynylcarbinol was converted into the β-carbomethoxyethyl ether of dimethylethynylcarbinol (I) by the method described previously [1].

Preparation of Hydrazide (II). A mixture of 64 g (0.38 M) of the β-carbomethoxyethyl ether of dimethyl-ethynylcarbinol, 20 g (0.4 M) of hydrazine hydrate, and 50 ml of absolute ethyl alcohol was boiled under a reflux condenser for 15 hours. The low-boiling fractions were distilled off on a water bath under the vacuum of a water-jet pump. 64 g of hydrazide (II) was obtained as a colorless, viscous oil.

Preparation of Azide (III) and Urethan (IV). A solution of 30.6 g (0.18 M) of hydrazide (II) in 35 ml of water was added with stirring at 0-5°C to a mixture of 16 ml of concentrated sulfuric acid, 72 ml of water, and 100 ml of ether. At 5-8° with stirring, a solution of 12.42 g (0.18 M) of sodium nitrite in 35 ml of water was then added. The ethereal layer was removed, and the aqueous layer saturated with ammonium sulfate and extracted three times with ether; the ethereal layer was united with the ethereal extract and dried with sodium sulfate. The ethereal solution of azide (III) was added to 50 ml of absolute ethyl alcohol, the ether distilled off, and the solution boiled for 2.5 hours. The alcohol was distilled off on a water bath under the vacuum of a water-jet pump. 30.1 g of urethan (I) was obtained as a viscous, light-brown oil.

Preparation of Amine (V). a) A mixture of 10 g (0.05 M) of urethan (IV), 12 g of barium hydroxide, and 250 ml of methyl alcohol was boiled under a reflux condenser for 24 hours. After cooling the mixture, the precipitate was filtered off and washed on the filter with methyl alcohol. The filtrate was concentrated by evaporation and the residue extracted with ether. The ethereal solution was dried with sodium sulfate and distilled. 1.6 g of the β-aminoethyl ether of dimethylethynylcarbinol (V) was obtained, b.p. 154-157°; n_D^{20} 1.4414; d_4^{20} 0.9013; found MR 37.42; calculated MR 37.52. Found: C 66.37; 66.43; H 10.31; 10.49; N 10.78; 10.92%. $C_7H_{13}NO$. Calculated: C 66.14; H 10.23; N 11.02%.

The picrate was prepared, m.p. 162-164° (from alcohol). Found: N 15.81; 15.85%. $C_{13}H_{16}N_4O_8$. Calculated: N 15.73%.

b) Into a round-bottomed flask, fitted with a Wurtz splashhead and connected to a reflux condenser, were placed 140 g of calcium oxide, 40 g of urethan (IV), and 80 ml of water. The flask was heated on a burner flame until elimination of water ceased. The reaction flask was cooled, 60 ml of water was added to it, and the mixture again heated until water was fully eliminated. The distillates were united, saturated with potash, and extracted with ether a number of times. The ethereal solution was with sodium sulfate and distilled. 7.2 g of the β-amino ethyl ether of dimethylethynylcarbinol (V) was obtained, b.p. 73-76° (22 mm); n_D^{20} 1.4418.

SUMMARY

A method is proposed for preparation of the β-aminoethyl ether of dimethylethynylcarbinol from the β-cyanoethyl ether of dimethylethynylcarbinol.

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RUPTURE OF SULFIDES OF THE THIOPHENE SERIES BY SODIUM IN LIQUID AMMONIA

Ya. L. Gol'dfarb, M. A. Kalik, and M. L. Kirmalova

N. D. Zelinskii Organic Chemistry Institute, Academy of Sciences, USSR

During our investigation of sulfides of the thiophene series [1,2] there arose the necessity of finding a practicable method of dealkylating the alkylthienyl sulfides synthesized by us from thienyllithium, sulfur, and alkyl halides [1]. It had been known previously that alkylbenzyl sulfides are debenzylated by sodium in liquid ammonia [3], and later it was shown that the methyl group is readily split off from methyphenyl sulfides under the same conditions [4,5]. Instead of liquid ammonia, pyridine [4] and alcohol [6] are also used. Similar experiments have not been carried out with sulfides of the thiophene series.

We have investigated the action of sodium in liquid ammonia and in alcohol on benzyl-(5-ethyl-2-thienyl) sulfide* and the action of sodium in liquid ammonia on methyl- and ethyl-2-thienyl sulfides and ethyl-(5-ethyl-2-thienyl) sulfide. All these alkylthienyl sulfides were readily dealkylated, and the corresponding mercaptans obtained in good yield. Benzyl-(5-ethyl-2-thienyl) sulfide is ruptured in liquid ammonia much more slowly, with high consumption of sodium and with inferior yields of mercaptan. Performance of this reaction in alcohol did not improve yields. Lithium in tetrahydrofuran, under the conditions described by Gilman and coworkers [7], reacted very vigorously with ethyl-(5-ethyl-2-thienyl) sulfide, also splitting off an ethyl group from the sulfide sulfur, but the reaction was accompanied by considerable resinification and mercaptan yield was insignificant.

EXPERIMENTAL

Rupture of Methyl-2-thienyl Sulfide. 5.0 g (0.04 M) of sulfide in 10 ml of dry ether was added to 50 ml of liquid ammonia. At a temperature of -60 to -70°C in a stream of dry nitrogen with stirring, 1.8 g (0.08 M) of metallic sodium was added in small portions. The blue color of the solution quickly disappeared and persisted only toward the end. Cooling was discontinued, excess sodium decomposed with a small quantity of ammonia chloride, and the ammonia evaporated off in a current of nitrogen. The residue was mixed with 20 ml of peroxide-free ether, 10 ml of methanol, and 50 ml of water. The ethereal layer was removed, the aqueous layer extracted with ether and acidified with 4N hydrochloric acid to pH 6. The resulting oil was extracted with ether, the ethereal extract washed with sodium bicarbonate solution and water, and dried with magnesium sulfate. The ether was distilled off in a stream of nitrogen. The residue (3.4 g, yield 79%) gave a positive reaction for the mercapto group and distilled at 69-70° (14 mm). The product darkened rapidly on storage. B.p. for 2-thienylmercaptan is given in the literature [8] as 54° (5 mm).

2,4-Dinitrophenyl-2'-thienyl Sulfide. A mixture of solutions of 0.8 g (0.007 M) of 2-thienylmercaptan in 25 ml of absolute alcohol, 0.26 g (0.0065 M) of caustic soda in 2 ml of water, and 1.4 g (0.007 M) of 2,4-dinitrochlorobenzene in 10 ml of absolute alcohol was boiled for 10 minutes and filtered while hot. On cooling, a crystalline substance precipitated; it was filtered, washed with absolute alcohol, and dried. 1.7 g (yield 85%) of sulfide was obtained, m.p. 116-117°. After recrystallizing from absolute alcohol, m.p. was 118-118.5°. M.p. for the sulfide is given in the literature [9] as 119°. Found: C 42.42; 42.68; H 2.25; 2.11; S 22.45; 22.64%. $C_{10}H_6N_2O_4S_2$. Calculated: C 42.54; H 2.14; S 22.72%.

*Obtained by the method described by us previously [1]; b.p. 145°C (3 mm); d^{20}_4 1.1188; n^{20}_D 1.6046.

Sulfide used	Molar ratio of sodium to sulfide, and solvent	Mercaptan obtained	Yield of mercaptan, %
Ethyl-2-thienyl sulfide	2 Liquid ammonia	2-Thienylmercaptan	77
Ethyl-(5-ethyl-2-thienyl) sulfide	2 Liquid ammonia	5-Ethyl-2-thienyl-mercaptan*	82
Benzyl-(5-ethyl-2-thienyl) sulfide	4.6 Liquid ammonia	5-Ethyl-2-thienyl-mercaptan	56.3
Benzyl-(5-ethyl-2-thienyl) sulfide	13.4 Absolute alcohol**	5-Ethyl-2-thienyl-mercaptan	54***

* 5-Ethyl-2-thienylmercaptan, b.p. 84° (13 mm); a description of its synthesis from 2-ethylthiophene will be published later. 2,4-Dinitrophenyl-(5-ethyl-2-thienyl) sulfide, m.p. 128°.

** At room temperature for an hour.

*** 38% of the initial sulfide was recovered.

Data on the rupture of other sulfides of the thiophene series is given in the table.

SUMMARY

By the action of sodium in liquid ammonia, alkylthienyl sulfides are readily dealkylated with formation of the corresponding mercaptans of the thiophene series.

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A NEW SYNTHESIS OF CYCLOPENTADECANONE (EXALTONE)

S. Z. Taits and Ya. L. Gol'dfarb

N. D. Zelinskii Institute of Organic Chemistry Academy of Sciences USSR

Previously [1,2] we showed the possibility of using the high reactivity of thiophene for the synthesis of macrocyclic systems by reactions of intramolecular acylation and acyloin condensation. In this work we describe a method of synthesis of exaltone by the following path:
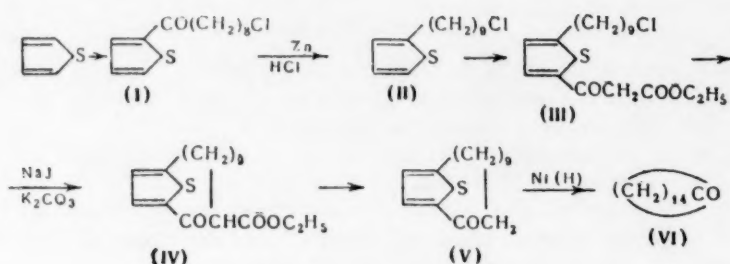
As this scheme shows, we have used here, for the formation of the side chain, the ω-chloroalkanoic acid which is now completely available due to the work of Nesmeyanov and co-workers [3] in the field of telomerization of ethylene.

By acylation of thiophene in the presence of $SnCl_4$ we have obtained 8-chlorooctylthienyl ketone (I) with a yield of 78%. (I) was reduced to 9-chlorononylthiophene (II) which by acylation with $C_2H_5OOCCH_2COCl$ [4] gave 2-(9-chlorononyl)-5-carbethoxacetylthiophene (III) with a yield of 71%. (III) was converted to 2-(9-iodononyl)-5-carbethoxyacetylthiophene from which by cyclization in methylethyl ketone over finely divided potash using the technique of high dilution (see, for example, [2]) we obtained the ketoester (IV). A similar method of intramolecular splitting of hydrogen halide was used successfully, earlier, [5] for obtaining a cyclic compound. In our case the yield in the step of cyclization was 67%; actually it was evidently higher since distillation of the reaction product even in a vacuum of 0.15-0.2 mm was accompanied by strong decomposition. The 2-carbethoxy-(11)-α-cyclothien-1-one* (IV) was purified by distillation in a vacuum of the order of 10^{-5} mm. By ketone splitting of (IV) we obtained (V), (II)-α-cyclothien-1-one, with a yield of 87%. If the cyclization was carried out without intermediate isolation of the iodide and the undistilled cyclization product was submitted to ketone splitting, then the yield of (V) was 49% based on (III). Reductive desulfurization of (V) with skeletal nickel gave exaltone (VI) with a yield of 75%.

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* The nomenclature of macrocyclic compounds which include a thiophene ring is discussed in [2].

If we consider that exaltone was previously obtained by pyrolysis of salts of the corresponding dicarboxylic acid with a maximum yield of 9.6% [6], by the method of Ziegler with a yield of 30-40% [7], and by acyloin condensation with a yield on the order of 50% [8], then it becomes clear that our method both as to yield (43.5% considered on the III) and as to simplicity of operation can be considered preparative.

EXPERIMENTAL

8-Chlorooctylthienyl ketone (I). Fifteen g of thiophene was acylated by 40 g of $Cl(CH_2)_8CO_2Cl$ [3] in 150 ml of C_6H_6 in the presence of 23.2 ml of $SnCl_4$ at -3 to 3°. Decomposition was carried out at 5° by adding 110 ml of HCl(1:10). Vacuum distillation gave 36 g of (I) with b.p. 167-169° (1.7 mm), n_D^{20} 1.5323; d_4^{20} 1.1089; found MR 72.38; calculated MR 72.49; yield 78%; Found: C 60.18; 60.15; H 7.32; 7.12%. $C_{13}H_{19}ClOS$. Calculated: C 60.30; H 7.34%. Semicarbazone of (I) had m.p. 101.5-102.5° (from aqueous CH_3OH). Found: C 53.52; 53.70; H 7.07; 6.94; N 13.01; 12.86%. $C_{14}H_{22}ClN_3OS$. Calculated: C 53.23; H 6.99, N 13.3%.

9-Chlorononylthiophene (II) was obtained by reduction of 65 g of (I) with 260 g of Zn turnings in a mixture of 195 ml of water, 390 ml of alcohol, and 260 ml of concentrated HCl (two hours at 20°, and one hour boiling). After dilution with water, extraction, and distillation we obtained 41.1 g of (II) with b.p. 126.5-131° (0.7 mm), n_D^{20} 1.5080; d_4^{20} 1.0271; found MR 71.03; calculated MR 71.23; yield 66%. Found: C 64.19; 64.05; H 8.66; 8.79; Cl 14.82; 14.91; S 12.82; 12.61%. $C_{13}H_{21}ClS$. Calculated: C 63.78; H 8.69; Cl 14.48; S 13.09%.

2-(9-Chlorononyl) 5-carbethoxyacetylthiophene (III). We acylated 45.8 g of (II) with 48.5 g of $C_2H_5OOCCH_2COCl$ [4] in 525 ml of C_6H_6 in the presence of 26.2 ml of $SnCl_4$. After decomposition of the reaction mass with 660 ml of dilute (1:10) HCl and distillation of the solvent we obtained by low temperature crystallization from ether 46.9 g of (III) with m.p. 30.6-31.3°, yield 71.5%. Found: C 60.51; 60.27; H 7.71; 7.51%. $C_{18}H_{27}ClO_3S$. Calculated: C 60.24; H 7.58%.

2-(9-Iodononyl)-5-carbethoxyacetylthiophene was obtained by boiling (III) with excess NaI in acetone or methylethyl ketone. Yields, 81 and about 100%, respectively; the product was purified by low temperature crystallization from ether; m.p. 29.5-30.7°. A mixed sample with (III) melted at 20-22°. Found: C 47.85; 48.06; H 6.09; 5.86%. $C_{18}H_{27}IO_3S$. Calculated: C 48.00; H 6.04%.

Cyclization of 2-(9-iodononyl)-5-carbethoxyacetylthiophene. We added 5.65 g of the latter in 500 ml of methylethyl ketone in the course of 30 hours and with the technique of high dilution to a boiling mixture of 1300 ml of methylethylketone and 200 g of finely ground potash. The mixture was boiled for eight hours, filtered, the potash was repeatedly washed with methylethyl ketone and was then dissolved in water and the layer of methylethyl ketone was distilled off and 5.41 g of cyclization product (a thick yellow oil) was distilled in a vacuum; b.p. 189-192° (0.15-0.2 mm) (strong decomposition). We obtained 2.7 g of product (yield 67%). Distillation of the reaction product in a high vacuum ($3 \cdot 10^{-5}$ mm) gave a glassy, almost colorless substance (temperature in the bath 155°) which from the analysis and molecular weight corresponded to 2-carbethoxy-(11)-α-cyclothien-1-one(IV); found* molec. wt. 321, 326; calculated molec. wt. 322.4 Found: C 66.62; 66.74; H 8.01; 8.07%. $C_{18}H_{26}O_3S$. Calculated: C 67.06; H 8.13%.

(11)-α-Cyclothien-1-one (V). We boiled 3.7 g of (IV) for eight hours with a solution of 20 ml of concentrated HCl in 80 ml of CH_3OH. After dilution with water, extraction, and distillation of the ether, we obtained 2.5 g (yield 87%) of a substance with m.p. 45-46.2 (from hexane). Found: C 72.08; 71.83; H 8.80; 8.63; S 12.65; 12.67%. $C_{15}H_{22}OS$. Calculated: C 71.97; H 8.87; S 12.82%. The semicarbazone of (V) had m.p. 193.4-194.5° (from alcohol). Found: C 62.49; 62.78; H 8.10; 8.10; S 10.35; 10.32; N 13.27; 13.50%. $C_{16}H_{25}ON_3S$. Calculated: C 62.5; H 8.19; S 10.67; N 13.67%.

On similar splitting of 7.74 g of undistilled cyclization product obtained without intermediate isolation of the iodide, from 10 g of (III) we isolated 3.4 g of (V) with b.p. 127.5-132° (0.05 mm) and m.p. 41-43°; yield on the initial (III) 49%.

Exaltone (VI). Two g of (V) in a mixture of 150 ml of alcohol and 60 ml acetone was stirred with 9 g of skeletal nickel at about 20° to a negative test for sulfur. The nickel was filtered off and after distillation of the solvent, the product was crystallized from alcohol. We obtained 1.35 g of (VI) with m.p. 63.5-64°; yield 75.2%. Found: C 80.07; 80.30; H 12.47; 12.36%. $C_{15}H_{28}O$. Calculated: C 80.29; H 12.58%. The semicarbazone had m.p.

* The molecular weight was determined by the distillation method [9].

184.5-186.5°. Found: N 14.76; 15.01%. $C_{16}H_{31}ON_3$. Calculated: N 14.92%. The literature gives for exaltone: m.p. 187-188° [6], 189-190° [11].

SUMMARY

We have worked out a new method of synthesis for exaltone by cyclization of 2-(9-halononyl)-5-carbethoxy-acetylthiophene, ketone splitting of the resulting macrocyclic ketoester into a acrocyclic ketone of the thiophene series, and reductive desulfurization of the latter into exaltone.

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TWO PATHS FOR THE DEHYDRATION OF 1,4-BUTANDIOL
TO DIVINYL WITH A TRICALCIUM PHOSPHATE CATALYST

L. Kh. Freidlin and V. Z. Sharf

N. D. Zelinskii Institute of Organic Chemistry Academy of Sciences USSR

The complete dehydration of 1,4-butandiol to divinyl has been carried out on an industrial scale by sodium phosphate deposited on coke. The conversion to divinyl at 280° was 20-30% with one passage [1]. In the patent literature there are also recomendations as catalysts of aluminum and chromium oxides, calcium chloride and dicalcium phosphate [2]. For partial dehydration of 1,4-butandiol into tetrahydrofuran there are suggestions of phosphoric acid [3] and for phosphates, chlorides, sulfates and oxides of metals, silica gel, and others [4], and of cation exchange resins [5]. These data do not give a clear idea of the conditions in which butandiol undergoes partial dehydration to tetrahydrofuran and the path for its complete dihydration to divinyl. The latter could occur through tetrahydrofuran (I), and also through butenol (II), according to the scheme:
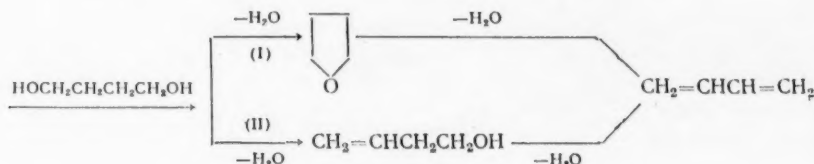
In the present work we have studied the stepwise dehydration of 1,4-butandiol in the presence of a tricalcium phosphate catalyst which is active in the dehydration of aliphatic alcohols [6]. The experiments were carried out on a flow apparatus [6]. The volume of catalyst was 25 ml, grain diameter 2×3 mm. After the experiments the catalyst was regenerated in a stream of air at 400-450°. The 1,4-butandiol used had b.p. 106° (5 mm), n_D^{20} 1.4478; d_4^{20} 1.015, and the tetrahydrofuran had b.p. 64-65°, n_D^{20} 1.4075; d_4^{20} 0.8878. In each experiment we passed over the catalyst 15-20 ml of dehydrating substance at a rate of 17.5 ml/hr. The liquid reaction products were fractionated in a column with 12 theoretical plates. In the resulting fractions were determined the content of carbonyl groups (by oxime formation) and unsaturated bonds (bromometrically). The position of the double bonds was determined by the KRS method. Gaseous products were analyzed chromatographically on aluminum oxide. We also considered the volume of dissolved gases which were evolved from the catalyst by heating.

The results showed that up to 320° there was exclusively selective occurrence of reaction I: the yield of tetrahydrofuran reached 98% of the theory (Fig. 1, curve 1), and gas formation was absent. At 336° the yield of gas was 14%, and at 426°, 73%, taking the evolved gas as divinyl (Fig. 1, curve 2). In the gaseous products of the experiment at 426° we determined, in %: C_4H_6 64.5, C_4H_8 4.9, C_4H_{10} 0.2, C_3H_6 16.9, C_3H_8 0.4, C_2H_4 2.3, C_2H_6 0.8, CH_4 0.9, CO 4.1. As we see, the gas contained only 64.5% divinyl; the rest were products of side reactions.

If the dehydration of butandiol to divinyl occurs through step I, then we would expect that at temperatures above 320° in the liquid catalyzate there would be found only water and tetrahydrofuran. However, it was shown

that in the catalyzate of experiments carried out at 336-426° besides tetrahydrofuran and water there were other reaction products present. In the table we give the results of distillation of the catalyzate (after drying over ignited potash) from experiments carried out at 336°. The table shows that in the catalyzate we found 47.5% tetrahydrofuran (fractions I and II). From fraction III we obtained a 2,4-dinitrophenylhydrazone with m.p. 123° whose mixed m.p. with the hydrazone of butraldehyde showed no melting point depression. Fractions V and VI were combined

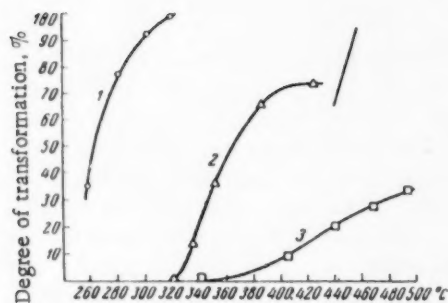| Fraction	B.p., °C	Amount of fraction in %	$n_D^{22.5}$	Content of carbonyl-containing compounds, calculated as butyral-dehyde, %	Content of unsaturated compounds calculated as butenol, %
I	61—62,5	14,9	1,4005	8,8	0,3
II	62,5—65	32,6	1,4042	1,0	0,0
III	67—97	8,2	1,4090	8,3	18,7
IV	97—112	4,8	1,4190	6,1	78,6
V	112—115	20,6	1,4210	0,5	92,1
VI	115—120	8,2	1,4275	1,0	96,0
Residue		6,2	—	—	—

Fig. 1. Effect of temperature of dehydration of 1,4-butandiol and tetrahydrofuran: 1) dehydration of 1,4-butandiol in tetrahydrofuran. Conversion into gaseous products: 1,4-butandiol (2) and tetrahydrofuran (3).

and submitted to repeated fractionation. We then again obtained two fractions with similar properties (I: b.p. 113-115°, n_D^{20} 1.4240; d_4^{20} 0.8676 and II: b.p. 115°, n_D^{17} 1.4260; d_4^{20} 0.8460), close to the properties of 1-buten-4-ol which according to the literature [7] has: b.p. 112-113.5°, n_D^{20} 1.4244; d_4^{20} 0.8475. The content of unsaturated alcohol in both fractions, determined by the bromine number, was 93.5-94%, by the method of acetylation in pyridine (in the cold) was 93.5-94%, and by the hydrogen number (hydrogenation over skeletal nickel at 20°), 100%. In study of the spectrum of the KRS fraction I we observed a frequency 1643 [6] characteristic for 1-buten-4-ol and a frequency 1677 of (I) characteristic for 2-buten-4-ol. The butyraldehyde formed at higher temperatures is probably the product of an isomerization reaction of 2-buten-4-ol. The latter, in turn, can be formed from 1-buten-4-ol.

It remains unsettled how the butenol is formed at higher temperatures: by isomerization of tetrahydrofuran or directly from butandiol. For a study of this question we investigated the behavior of tetrahydrofuran at 340-494° (Fig. 1, curve 3). We showed that at 340° gases are absent, and tetrahydrofuran is recovered unchanged. Hence, its isomerization to butenol does not occur. Marked gas formation begins only at temperatures above 400°. At 406° the yield of gas is 9%, and at 494°, 34%, assuming the evolved gas to be divinyl. The composition of the gaseous reaction products at 440° in % is C_4H_6 46.7, C_4H_8 5.8, C_4H_{10} 0.4, C_3H_6 23.0, C_3H_8 2.2, C_2H_4 6.0, C_2H_6 2.6, CH_4 4.2, H_2 5.2, CO 5.5. In the catalyzates from the experiments at 406-494° we found only tetrahydrofuran and water. Thus, tetrahydrofuran begins to undergo catalytic transformation into divinyl and other gaseous products at temperatures which are almost 100° higher than those at which gas is formed from 1,4-butandiol. It follows from these results that at temperatures above 320° there is a change in reaction mechanism, producing a second direction of dehydration of butandiol which evidently takes place with a considerably higher temperature coefficient than direction I. Hence, in this process divinyl is basically formed through butanol and not through tetrahydrofuran as was indicated in [1].

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SUMMARY

1. In the temperature interval 260-320° on a tricalcium phosphate catalyst 1,4-butandiol is selectively dehydrated to tetrahydrofuran. At temperatures above 320° from butandiol along with tetrahydrofuran there is formed 1-buten-4-ol, butyric aldehyde, divinyl, and other gaseous products.

2. Tetrahydrofuran is not isomerized into butenol at 340° and begins to be converted to divinyl at temperatures which are almost 100° higher than the temperature of initial dehydration of 1,4-butandiol to divinyl.

3. Above 320° 1,4-butandiol is dehydrated simultaneously in two directions: into tetrahydrofuran and into butenol, but divinyl is formed chiefly from the latter.

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A NEW METHOD OF SYNTHESIS OF N,N-DIBENZYL-DL-PHENYLALANINE AND N,N-DIBENZYL-DL-ALANINE

K. T. Poroshin and Vyach. I. Maksimov

N. D. Zelinskii Institute of Organic Chemistry Academy of Sciences, USSR

The well known process for obtaining N,N-dibenzyl-α-amino acids [1], consisting of benzylating α-amino acids by the action of benzyl chloride on them in aqueous-alcoholic alkali produces benzylation simultaneously on the amino and carboxyl groups. The resulting benzyl esters of N,N-dibenzyl-α-amino acids are then saponified by boiling with alkali, in some cases at 120°. Such treatment of the α-amino acids leads to their complete racemization. Hence, the chief obstacle for the use of a benzyl protector in the synthesis of peptides is the slight availability of the optically active N,N-dibenzyl-α-amino acids. Only one method has been described for isolating the L-isomer from the racemate [1] with the help of threo-1-(p-nitrophenyl)-2-amino-1,3-propandiol. Along with this, as compared to other prevailing methods of protection, the dibenzyl method has the following advantages: 1) its exclusive stability with respect to hydrolytic agents; 2) the ability to form salts with different acids, which permits us always to obtain crystalline derivatives of N,N-dibenzyl-α-amino acids and N, N-dibenzylpeptides; 3) the possibility of removing the protective groups by hydrogenation over Pd black a reaction which at the same time does not take place with HBr·CH$_3$COOH; this permits combining the protective group with the benzyl esters in the synthesis of peptides, etc.

In the present work we describe the preparation of N,N-dibenzyl-α-amino acids through their benzyl esters by treatment of the latter with HBr in glacial CH$_3$COOH. We have studied the reaction of hydrobrominolysis of the benzyl esters of N,N-dibenzyl-DL-alanine and N,N-dibenzyl-DL-phenylalanine at various temperatures and degrees of saturation of glacial CH$_3$COOH by hydrogen bromide. We should remark that hydrobrominolysis occurs under mild conditions (room temperature).

We have shown that the hydrobrominolysis reaction

$$\begin{array}{c} C_6H_5CH_2 \\ C_6H_5CH_2 \end{array}\!\!\!\!>\!\!N-\overset{\overset{\displaystyle R}{|}}{C}H-COOCH_2C_6H_5 \xrightarrow{\ HBr\cdot CH_3COOH\ }$$

$$\longrightarrow C_6H_5CH_2Br + \begin{array}{c} C_6H_5CH_2 \\ C_6H_5CH_3 \end{array}\!\!\!\!>\!\!\underset{\overset{\displaystyle .}{HBr}}{N}-\overset{\overset{\displaystyle R}{|}}{C}H-COOH$$
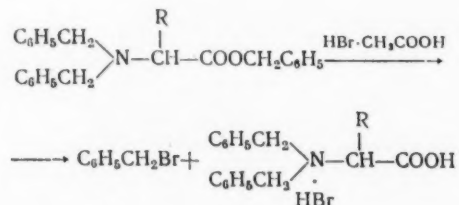
occurs at room temperature in a straight forward manner (see the electrophoretogram) without removing the benzyl groups from the nitrogen. Treatment of the benzyl ester of N,N-dibenzyl-DL-phenylalanine with glacial acetic acid saturated with HBr at room temperature for 5-6 days leads to formation of pure N,N-dibenzyl-DL-phenylalanine (hydrobromide). It should be noted that the dibenzyl amino acid hydrobromide can be used directly in the synthesis of peptides. When the ester is boiled in glacial CH$_3$COOH saturated with HBr, as shown by paper

electrophoresis, the benzyl group begins to be removed from the nitrogen and a mixture of substances is formed: the benzyl ester of dibenzylphenylalanine, dibenzylphenylalanine, benzylphenylalanine, and phenylalnine. In the case of DL-alanine ·his reaction occurs fully and straightforwardly when the corresponding ester is boiled in HBr ·CH₃COOH (d = 1.270) for 45 minutes.

It is known [2] that hydrobrominolysis of the $C_6H_5CH_2OCO$ group occurs in about 15 minutes for the benzyl esters of amino acids and in about 12 hours for peptides. In comparison with these results we see the increased stability of the ester bond in benzyl esters of N,N-dibenzyl-α-amino acids with respect to hydrobrominolysis; increased stability is also found for saponification by alkali. N,N-dibenzyl- DL-alanine and N,N-dibenzyl-DL-phenylalanine, like N,N-dibenzyl-DL-leucine [3] under the action of PCl_5, $POCl_3$, $SOCl_2$, and $COCl_2$ form unstable acid chlorides.

EXPERIMENTAL

Synthesis of N,N-dibenzyl-DL-phenylalanine. Thirteen g of DL-phenylalanine and 15 g of NaOH were dissolved in a mixture of 60 ml of alcohol and 100 ml of water. In the course of 10-15 minutes with boiling we added 40 ml of $C_6H_5CH_2Cl$ and continued the boiling for 30-40 minutes. After cooling, we added chloroform; the organic layer was evaporated in a vacuum (100°, 12-15 mm Hg). We added to the remaining mass a small amount of HBr ·CH₃COOH and then a mixture of ether and chloroform (about 8:2); a precipitate of the crystalline hydrobromide of the benzyl ester of N,N-dibenzyl-DL-phenylalanine appeared (34 g, that is, 84%, m.p. 151°). Thirty g of the latter was treated with 20 ml of glacial CH₃COOH saturated with HBr; after seven days it was evaporated dry (80%, m.p. 171-172°); the hydrobromide was treated with 50 ml of concentrated NH_4OH and 250 ml of water and left standing over night, then was acidified with a large volume of dilute CH₃COOH. The total yield based on starting phenylalanine was 60%, m.p. 116-117°, calculated: C 80.00; H 6.66; N 4.58%. Found: C 80.13; 80.08; H 6.86; 6.78%; N 4.18; 4.22; 4.34%. The substances was soluble in organic solvents except for ligroin, in CH₃COOH (dilution with water precipitated it), in HCl and alkalis, and quite soluble in ammonia. When dibenzylphenylalanine was boiled in isoamyl alcohol with $CuCO_3$, water and a slight impurity of CH₃COOH an intensely green solution formed from which, after standing a week, a violet-red precipitate came down and the solution was decolorized. When this precipitate was heated in isoamyl alcohol it again formed a green solution from which the red-violet precipitate again appeared on cooling.

Line of deposit

Fig. 1. Electrophoretogram. Solvent 30% CH₃COOH; gradient about 9 v/cm. Hydrobrominolysis of the benzyl ester of dibenzylphenylalanine (at room temperature). Time of hydrobrominolysis: I) 4 hours; II) 40 hours, III) 53 hours, IV) 136 hours, V) 0 hours (starting substance). Time of electrophoresis: I) 3 hours 10 minutes; II) 3 hours; III) 3 hours, 15 minutes; IV) 5 hours; V) up to 16 hours.

The hydrobrominolysis used in this synthesis was studied by paper electrophoresis (Fig. 1). In the electrophoresis of the benzyl ester of dibenzylphenylalanine in 30% CH₃COOH it remained nonmobile; the dibenzylphenylalanine moved to the cathode.

On boiling with glacial CH₃COOH saturated with HBr the benzyl group began to be removed from the nitrogen and there appeared on the electrophoretogram spots of benzylphenylalanine (these migrated twice as fast as dibenzylphenylalanine), and phenylalanine (three times as fast). In treatment with ninhydrin the phenylalanine, developed first as a violet spot, then the yellow-orange benzylphenylalanine, and with strong and long heating, the yellow spot fo dibenzylphenylalanine.

Synthesis of N,N-dibenzyl-DL-alanine. This synthesis was carried out without separation of the benzyl ester. To 15 g of DL-alanine and 30 g of NaOH was added 0.5 liters of 80% isopropyl alcohol and 100 ml of benzyl chloride; the mixture was boiled for three hours; the NaCl which precipitated was filtered off and the mother liquor was evaporated in a vacuum (100°); to the mass which remained was added 160 ml of HBr·CH₃COOH (d = 1.270), it was boiled for 45 minutes; the crystals of NaBr which precipitated on cooling were filtered off, the mother liquor was evaporated dry; the crystalline substance was washed with 300-400 ml of water (pH not less than 7),

ether was added and the mixture left over night, filtered and washed several times more with ether (yield 53 g, that is, more than 90%; after recrystallization from water, m.p. 131-134°). To the precipitate was added a large volume of ether and a stream of NH_3 was passed in until the odor remained; the precipitate was filtered and washed several times with ether (about 2 liters). After evaporation of the ether we obtained dibenzylalanine; yield 28 g (62%); m.p. 96-98°. The literature gives [1]: m.p. 96-98°, b.p. 230-235° (16 mm), and in distillation the condensate is somewhat tarry.

A small amount of toluene was added to the distilled substance and after several days the crystals were filtered off. Calculated: C 75.83; H 7.34; N 5.20%. $C_{17}H_{19}NO_2$. Found: C 75.80; 75.67; H 7.14; 7.22; N 5.41; 5.51%.

Electrophoretically the substance was homogeneous, migrating like the other dibenzylamino acids. The substance was soluble in methanol, chloroform, ethyl acetate, less so in ether, poorly in ligroin. When boiled in chloroform with $CuCO_3$ and water, it gave a crimson chloroform solution. With PCl_5 in chloroform at room temperature it actively evolved an equivalent volume of gas (CO, burned with a blue flame, not absorbed by alkali).

SUMMARY

1. We have synthesized by a new method N,N-dibenzyl-DL-alanine and N,N-dibenzyl-DL-phenylalanine.

2. We have studied the reaction of hydrobrominolysis of the benzyl esters of these amino acids.

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THE VALUE OF THE SECOND DISSOCIATION CONSTANT
OF HYDROGEN SULFIDE

S. S. Zavodnov and P. A. Kryukov

Hydrochemical Institute, Academy of Sciences USSR

The determination of the second dissociation constant of hydrogen sulfide was undertaken by us in connection with a study of the state of hydrogen sulfide in thermal mineral waters. Although for the value of the first dissociation constant of hydrogen sulfide K_{1H_2S}, there were recently obtained reliable values over a wide temperature range [1], there are no sufficiently exact data yet for the values of K_{2H_2S}. For determination of K_{2H_2S} different methods have been used based on study of the solubility of sulfides [2-4], decrease in freezing point of Na_2S solutions [5,6], determination of the concentration of hydroxyl ions [3,7] and pH values in solutions of salts of hydrogen sulfide [8-10]. The most exact results would be expected from use of the latter method. However, the measurements needed here of the pH values in strongly alkaline solutions (in the region pH > 11) were until recently connected with great difficulties due to the alkaline errors given by glass electrodes made of glass with the ordinary composition ES-1 (Corning 015).

Kubli [8], and also Tumanova, Mishchenko, and Elis [10], using such glass electrodes for measurement of the pH in solutions of hydrogen sulfide salts, made considerable corrections in their observed values.* In connection with these difficulties Konopik and Leberl [9] measured the value of the pH of Na_2S solutions colorimetrically but their accuracy was insufficient especially since decolorization of the indicator occurred. In recent years a composition of electrode glass had been worked out [11,12] which is suitable for measuring in a strongly alkaline region and at high temperatures, and there are also recipes for corresponding buffer solution [13,14]. This permits us to make a new attempt to determine the value of K_{2H_2S}.

EXPERIMENTAL

The method which we used consited in measuring the pH of solutions of Na_2S over a wide range of concentrations. The glass electrode was prepared from glass No. 106 worked out in the Department of Physical Chemistry of the Leningrad State University [12]. The electrode was calibrated with buffer solutions (potassium biphthalate, phosphate mixture, borax, and $Ca(OH)_2$) whose pH values from 0 to 60° were given in the work of Bates and coworkers [13-14]. The measurements were made with a PPTV-1 potentiometer amplified by a 6ZhlZh lamp [15] and with a mirror galvanometer. The measuring cell was placed in a wide mouthed Dewar vessel and was thermostatically controlled by circulating water from a TS-15 thermostat.

Recrystallization of Na_2S and all pH measurements in the Na_2S solutions were carried out in a stream of nitrogen which for purification was passed from the cylinder into a column of pyrophoric copper heated to 200° and then was passed through a wash vessel with a saturated solution of $Ba(OH)_2$ and of water.

Calculation of pK_{2H_2S} was carried out starting from the equation

$$pK_{2H_2S} + c\mu = pH - lg\frac{[S'']}{[HS']} + 1.5\sqrt{\mu}$$

(1)

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* In the work of Kubli incorrect calculations were made. We corrected the values of K_{2H_2S} at 20° to 12.88 instead of the given value of 12.44.

The essential characteristic in determination of the second dissociation constant of H_2S in comparison with the determination of the dissociation constant of a stronger acid, such as carbonic, is the difficulty in calculating the ratio $[S'']/[HS']$. Although in the case of carbonic acid the ratio $[CO_3'']/[HCO_3']$ is known accurately enough from the corresponding amounts of neutral and acid salt used with introduction of a small correction for hydrolysis of CO_3'', in the case of a solution of Na_2S all the HS' is formed as a result of hydrolysis of the S'' ion.

The ratio of $[S'']/[HS']$ was calculated by the pH value and the starting concentration of Na_2S as described below. In solutions of Na_2S the relations should hold:

$$[Na^{\cdot}] + [H^{\cdot}] = [OH'] + [HS'] + 2[S''] \tag{2}$$
$$\Sigma S = [H_2S] + [HS'] + [S''] \tag{3}$$

and

$$2\Sigma S = [Na^{\cdot}] \tag{4}$$

In the case considered we can neglect $[H^{\cdot}]$ and $[H_2S]$ as compared with $[Na^{\cdot}]$, $[HS']$ and $[S'']$. Substituting $[OH'] = (K_W \gamma_{H_2O})/(\alpha_H \cdot \gamma_{OH'})$ and solving equations (2,3,4) relative to $[S'']$ and $[HS']$ we get:

$$[S''] = \Sigma S - \frac{K_W \gamma_{H_2O}}{a_H \cdot \gamma_{OH'}}, \quad [HS'] = \frac{K_W \gamma_{H_2O}}{a_H \cdot \gamma_{OH'}} \tag{5}$$

The value of γ_{H_2O} at small concentrations of the solution is taken as equal to unity. Calculation of the ionic strength of solutions of Na_2S and $\gamma_{OH'}$ were made by the method of successive approximations. In the first approximation $[OH']_1$ was taken equal to $(K_W)/(\alpha_H)$, $[HS']_1 = [OH']_1$, $[S'']_1 = \Sigma S - [HS']_1$ and $[Na^{\cdot}] = 2\Sigma S$. The value obtained for μ_1, was used for calculation of $\gamma_{1OH'}$ by the Debye-Huckel equation. In the second approximation $[OH']_2$ was taken equal to $(K_W)/(\alpha_H \cdot \gamma_1 OH')$, $[HS']_2 = [OH']_2$, $[S'']_2 = \Sigma S - [HS']_2$ and $[Na^{\cdot}] = 2\Sigma S$. The resulting value of μ_2 was used for calculation of $\gamma_2 OH'$, etc. We were limited to three approximations.

If we represent graphically the values found by this process for the right part of equation (1) as a function of μ, we obtain a relation which is nearly linear. By extrapolation to a zero value of μ by the method of least squares we can find the values for $pK_2 H_2S$. In the table we give the experimental data for determination of pH in solutions of Na_2S, the values of $pK'_2 H_2S = pH - \lg [S'']/[HS] + 1.5\sqrt{\mu}$, and the values found by the method of least squares for the thermodynamic constant pK_{2H2S} as the results show, depends little on μ. The relation of the second dissociation constant of hydrogen sulfide to temperature can be expressed by the equation

$$pK_{2H_2S} = 12,93_4 - 0,016_5 (t - 20°)$$

Determination of pK_{2H2S}

T °C	ΣS (M/л)	pH	μ	pK'_{2H_2S}	pK_{2H_2S}	T °C	Σ (M/л)	pH	μ	pK'_{2H_2S}	pK_{2H_2S}
20	0,1050	12,54	0,2804	13,02	12,94	40	0,1012	12,08₈	0,2589	12,65	12,61
	0,0694	12,48₂	0,1795	12,97			0,06072	11,93₀	0,1479	12,62	
	0,0354	12,37	0,0856	12,95			0,03643	11,82₆	0,0839	12,62	
	0,0354	12,37	0,0856	12,95			0,02186	11,68₃	0,0480	12,60	
	0,0295	12,33₃	0,0699	12,96			0,01286	11,51₅	0,0273	12,62	
	0,0173	12,18₇	0,0392	12,92		50	0,1012	11,78₃	0,2545	12,51	12,43
	0,01616	12,18	0,0361	12,97			0,06072	11,71₀	0,1434	12,52	
	0,01140	12,07	0,0248	12,96			0,05060	11,65₈	0,1181	12,48	
	0,00812	11,95	0,0174	12,94			0,03643	11,58₂	0,0821	12,48	
	0,00654	11,88	0,0138	12,97			0,02530	11,47₈	0,0555	12,43	
30	0,05060	12,16₃	0,1229	12,82	12,76		0,02143	11,42₁	0,0464	12,44	
	0,03036	12,05₅	0,0699	12,81			0,01286	11,24₆	0,0269	12,43	
	0,02143	11,95₀	0,0482	12,76		60	0,1012	11,53₀	0,2550	12,25	12,28
	0,01822	11,91₅	0,0400	12,83			0,06072	11,45₁	0,1444	12,24	
	0,01286	11,79₈	0,0277	12,79			0,03643	11,34₇	0,0813	12,29	
	0,01093	11,74₁	0,0234	12,77			0,02143	11,18₀	0,0462	12,23	
	0,00772	11,61₂	0,0162	12,75			0,01286	11,01₅	0,0268	12,32	
							0,00772	10,82₂	0,0158	12,27	

SUMMARY

We have determined the second dissociation constant of hydrogen sulfide in the temperature range 20-60°.

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THE STEREOCHEMISTRY OF THE DIENE CONDENSATION
OF TRANS-1-VINYL-6-KETO-9-METHYL-Δ'-OCTALENE
WITH QUINONE AND THE SYNTHESIS OF DL-3β, 17aβ-
DIHYDROXY-18-NOR-D-HOMOANDROSTANE

I. A. Gurvich, T. V. Ilyukhina, and V. F. Kucherov

In a number of works relating to the synthesis of steroids and related substances by the diene condensation it was observed that the reaction of unsymmetrical vinylcyclenes with unsymmetrical dienophils led to a mixture of geometrical isomers [1-3] whose configurations in the case of such a reaction with a cis-compound would be determined by the nature of the screening diene system in the starting vinylcyclene. This was studied in more detail in the case of the condensation of trans-1-vinyl-6-keto-9-methyl-Δ'-octalene (I) with quinone [4]. On the basis of this molecular model it was suggested that the adduct (II) formed in largest amount had the configuration of an endo-cis-addition of quinone to the side opposite the angular methyl group of the diene. On this basis the synthesis of the diacetate of dl-18-nor-D-homo-Δ⁹ (11)-androsten-3,17a-diol (V) was carried out. However, the spacial structure of the synthesized product and hence also the stereochemistry of the diene synthesis itself in this case remained undisclosed in the end.
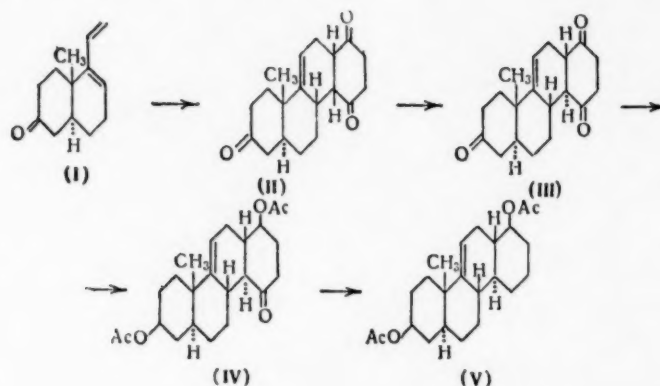
In order to solve both these questions unequivocally it was necessary by the use of these compounds to carry out the synthesis of such derivatives of 18-nor-D-homoandrostane as would have an established structure and configuration. Such a compound would be dl-3β,17β-dihydroxy-18-nor-D-homoandrostane (X), a stereospecific method for the preparation of which has recently been published by Johnson [5]. Starting from the ketodiacetate (IV), its synthesis was carried out by the following scheme based on the use of the known stereospecific transformation at the Δ^9 (11) double bond [6].

R=H, Ac
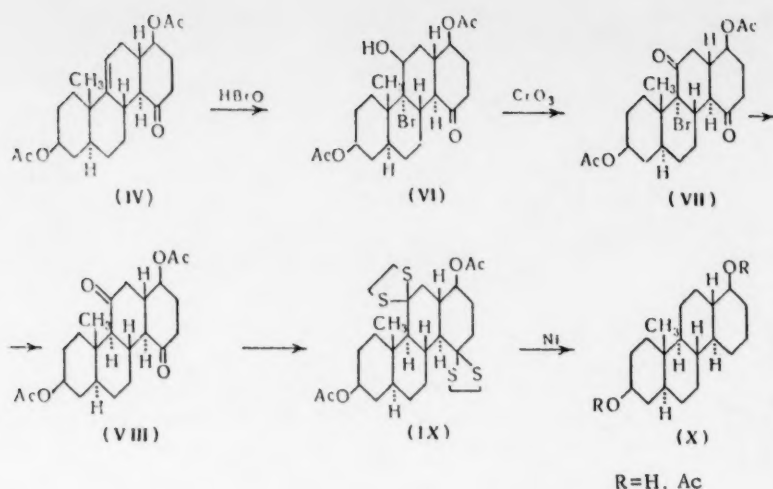
In this reaction of the ketodiacetate (IV) with hypobromous acid the bromohydrin (VI) is formed with a yield of 73%, and in accord with the method of its preparation has an axial arrangement of the bromine atom at C_9. By oxidation of the bromohydrin (VI) with chromic anhydride in acetic acid we obtained the bromodiketone (VII) with a yield of over 90% and this was reduced with zinc dust to the diketodiacetate (VIII). The infrared spectrum showed complete agreement of the oscillation frequency of the carbonyl group in the diketodiacetate (VIII) and the bromodiketone (VII) which indicates the axial position of the bromine in the latter [7]. In order to proceed to the required diol from the diketodiacetate (VIII) we obtained the dithioketal (IX) which on reduction with skeletal nickel in dioxane solution gave a total yield of 78% of the diacetate (X) (R= Ac); this was saponified to the corresponding diol (X) (R= H). Neither of these compounds gave depression of the melting point with known samples of dl-3β , 17aβ -diohydroxy-18-nor-D-homoandrostane and its diacetate, which was kindly presented by Prof. W. S. Johnson of the University of Wisconsin (U.S.) to whom we express grateful thanks. As a result of the described reactions we can consider as proven the structure and configuration of all the previously described [4] derivatives of 18-nor-D-homoandrostane obtained in the diene synthesis from trans-1-vinyl-6-keto-9-methyl-Δ'-octalene whose condensation with quinone took place by the principle of endo-cis-addition preferably on the side opposites the angular methyl group.

EXPERIMENTAL

Bromohydrin (VI). To a solution of 0.493 g of the ketodiacetate (IV) in 25 ml of dioxane was added 2 drops of 72% perchloric acid, 2.5 ml of water, and 0.413 g of N-bromoacetamide. Stirring was continued for 15 minutes in the dark at 20°. After addition of an excess water solution of Na_2SO_3 and 15 ml of water the precipitating crystals of bromide were filtered off, washed with water, and dried in a vacuum. We obtained 0.45 g of bromo-hydrin (VI) with m.p. 200° (from acetone). Found: C 57.10; 56.95; H 6.70; 6.74; Br 16.40; 16.70%. $C_{23}H_{33}O_6Br$. Calculated: C 56.91; H 6.80; Br 16.46%.

Diketodiacetate bromide (VII). A suspension of 0.280 g of bromohydrin (VI) in 45 ml of glacial acid was oxidized with a solution of 0.06 g of chromic anhydride in acetic acid. After the usual treatment we obtained 0.26 g of the bromodiketone (VII) with m.p. 191-192.5°(from acetone), ν (CHCl₃) 1719 cm^{-1}(K 3140), 1734 (K 2500). Found: C 56.94; 56.80; H 6.67; 6.66; Br 16.10; 16.30%. $C_{23}H_{31}O_6Br$. Calculated: C 57.13; H 6.46; Br 16.50%.

Diketodiacetate (VIII). To a solution of 0.140 g of bromodiketone (VII) in 12 ml of glacial acetic acid with heating on a boiling water bath and stirring was added 0.28 g of zinc dust in the course of 40 minutes, after which the zinc was filtered off, the solvent was distilled in a vacuum, and the reaction product was extracted with benzene. We obtained 0.09 g of diketodiacetate (VIII) with m.p. 157.5-158° (from methanol), ν (CHCl₃) 1719 cm^{-1} (K 3840), 1734 (K 2740). Found: C 68.15; 68.53; H 7.88%. $C_{23}H_{32}O_6$. Calculated: C 68.29; H 7.97%.

Diacetate (X) (R= CH₃COO-). To a solution of 160 mg of diketodiacetate (VIII) in 0.5 ml of dry dithioglycol was added 0.2 ml of boron trifluoride etherate. On the next day methanol was added to the reaction mass and we

isolated the dithioketal with m.p. 259-260°; this was boiled for eight hours with 2 g of skeletal nickel in dioxane. We obtained 115 mg of diacetate (X) (R=CH_3COO-) with m.p. 166-167° (from methanol), ν (CCl_4) 1734 cm^{-1} (K 2750), 1248 (K 4360). Found: C 73.31; 73.13; H 9.63; 9.64%. $C_{23}H_{36}O_4$. Calculated: C 73.36; H 9.64%. A mixed sample with known diol (X) gave no depression.

Diol (X) (R = H). To a solution of 70 mg of diacetate (X) (R = CH_3COO−) in 14 ml of methanol was added 80 mg of KOH in 1 ml of water and the mixture was boiled for 2.5 hours, after which the solution was neutralized with hydrochloric acid, the solvent was distilled off and water was added to the residue. We filtered off 55 mg of diol (X) (R = H) which after crystallization from aqueous methanol and acetone melted at 208-209°. Found: C 77.77; 77.79; H 10.91; 10.71%. $C_{19}H_{32}O_2$. Calculated: C 78.03; H 11.03%. A mixed sample with known diol (X) gave no depression.

SUMMARY

1. We have carried out a stereospecific synthesis of dl-3β, 17aβ -dihydroxy-18-nor-D-homoandrostane (X) and its diacetate by which we have showed the configuration and structure of the previously described derivatives of 18-nor-D-homoandrostane.

2. We have showed the spacial structure of the adduct (III) whose configuration corresponds to an endo-cis-addition of quinone to trans-1-vinyl-6-keto-9-methy-Δ'-octalene (I) on the side opposite the angular methyl group.

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THE DETERMINATION OF THE NUMBER OF NITRO GROUPS
IN POLYNITROALKANES

V. N. Slovetskii, V. A. Shlyapochnikov, K. K. Babievskii,
and S. S. Novikov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

In a previous study we showed experimentally that the extinction coefficients ϵ for the absorption maximum of nitro groups (about 280 mμ) in the ultraviolet absorption spectra are linearly related to the number of nitrogroups in the molecule of nitrocompound for mononitro, gem-dinitro, and trinitromethyl groups [1]. It seemed of interest to extend these findings to a wider number of polynitroalkanes including such compounds as those in which the nitro groups occurred on different carbon atoms.

EXPERIMENTAL

The ultraviolet absorption spectra were obtained on an SF-4 spectrophotometer in solutions in isooctane and methylene chloride. We studied the spectra of freshly prepared solutions of polynitroalkanes in concentrations of 0.6-1.0 g/liter. The results of the measurement are given in the table.

The average value of ϵ for one nitro group is 25 ± 2 [1], for two nitrogroups 56 ± 12, for three nitro groups 108 ± 2, and for four nitro groups 141 ± 6, that is, for all the compounds studied the relation of the extinction coefficient ϵ of the absorption maximum for the nitro group

$$\epsilon = \frac{D}{c \cdot l},$$

(where D is optical density, $\underline{c}$ concentration in moles per liter, $\underline{l}$ the length of the cuvette) to the number of nitro groups has a linear character (Fig.) which does not depend on the structure of hydrocarbon skeleton of the polynitroalkane and depends very little on the arrangement of the nitrogroups; this permits use of this regularity in analytical procedures for determining the number of nitro groups in polynitroalkanes.
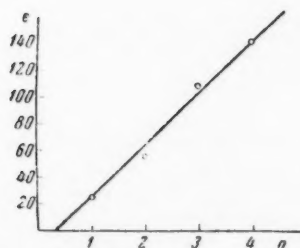
Dependence of extinction coefficient (ϵ) λ
about 280 mμ on number of nitrogroups (n).

SUMMARY

1. We have studied the ultraviolet absorption spectra of 14 polynitroalkanes which contain 2,3, and 4 nitro groups in various positions.

2. We have showed the possibility of determining the number of nitro groups by the ultraviolet spectra in polynitroalkanes which contain nitro groups on different carbon atoms.

Ultraviolet Absorption Spectra of Polynitroalkanes

Formula	Name of substance	M.p.,°C	No. of NO_2 groups	Position	Solvent	Maximum λ in mμ	ϵ
$O_2N-CH_2-CH_2-NO_2$	1,2-Dinitro-ethane	39—40	2	1,2	Methylene chloride	282 w	44
$O_2N-(CH_2)_4-NO_2$	1,4-Dinitro-butane	33—34	2	1,4	Isooctane	278 w	47
					Methylene chloride	278 w	47
$O_2N-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-NO_2$	1,3-Dinitro-2,2-dimethyl-propane	89—90	2	1,3	Isooctane	280 w	68
$CH_3-\overset{NO_2}{\underset{CH_3}{C}}-\overset{NO_2}{\underset{CH_3}{C}}-CH_3$	2,3-Dinitro-2,3-dimethyl-butane	213—214	2	2,3	Methylene chloride	283 w	65
$CH(NO_2)_3$	Trinitromethane	25	3	1,1,1	Isooctane	280 w	110
$CH_3-\overset{NO_2}{\underset{NO_2}{C}}-CH-CH_3$ NO_2	2,2,3-Trinitro-butane	47—48	3	2,2,3	Isooctane	282 w	108
$CH_3-\overset{NO_2}{\underset{NO_2}{C}}-CH-CH_2-NO_2$ C_2H_5	1,3,3-Trinitro-2-ethyl-butane	Liquid	3	1,3,3	Isooctane	280 w	110
					Methylene chloride	280 w	106
$C(NO_2)_4$	Tetranitro-methane	14,2	4	1,1,1,1	Methylene chloride	280 w	135
$CH_3-\overset{NO_2}{\underset{NO_2}{C}}-\overset{NO_2}{\underset{NO_2}{C}}-CH_3$	2,2,3,3-Tetra-nitrobutane	162,2—163	4	2,2,3,3	Methylene chloride	280 w	135
					Isooctane	277 w	144
$(O_2N)_3C-CH_2-CH_2-NO_2$	1,1,1,3-Tetra-nitropropane	51,5—52	4	1,1,1,3	Isooctane	277— 270 f	145
$(O_2N)_3C-CH_2-CH-CH_3$ NO_2	1,1,1,3-Tetra-nitrobutane	51—51,2	4	1,1,1,3	Isooctane	277 w	147
					Methylene chloride	270 w	138
$(O_2N)_3C-CH_2-CH-C_2H_5$ NO_2	1,1,1,3-Tetra-nitropentane	24,5—25	4	1,1,1,3	Isooctane	278 w	145
					Methylene chloride	281 w	142
$(O_2N)_3C-CH_2-CH-CH(CH_3)_2$ NO_2	1,1,1,3-Tetra-nitro-4-methylpentane	65—65,2	4	1,1,1,3	Isooctane	275 w	140
$(O_2N)_3C-CH_2-CH-C_3H_7$ NO_2	1,1,1,3-Tetra-nitro-hexane	37,7—38	4	1,1,1,3	Isooctane	274 w	140

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PREPARING AROMATIC SELENIUM COMPOUNDS THROUGH
THE ARYL DIAZONIUM BOROFLUORIDES

A. N. Nesmeyanov, V. N. Vinogradova and L. G. Makarova

Institute of Organic Chemisty of the Elements, Academy of Sciences, USSR

We have obtained aromatic compounds of a number of elements with the help of aryl diazonium borofluorides (see review of the literature in paper [1]). In the present work we report the synthesis of aromatic selenium compounds using aryl diazonium borofluorides.

Aromatic selenium compounds, diaryl selenides, diaryl diselenides, aryl selenocyanates, are obtained through the diazonium compounds by reaction of aryl diazonium chlorides and acetates with alkali selenides [2], diselenides [2], polyselenides [3], and potassium selenocyanate [4]. In the decomposition of aryl diazonium borofluorides by zinc dust in the presence of selenium tetrachloride in acetone we obtained diaryl selenides with the aryls: phenyl, p-and o-tolyl, p-chlorophenyl, and p-methoxyphenyl. In the case of arylphenyl we also obtained small amounts of diaryl diselenides. Here the yield was small; only in the cases the yield was lower. Diaryl selenides were isolated by vacuum distillation and with steam, and were identified also by their conversion to the dibromides.

EXPERIMENTAL

We obtained the diaryl selenides by decomposition of aryl diazonium borofluorides in the presence of zinc dust and selenium tetrachloride by the same general method: a suspension of selenium tetrachloride in absolute acetone was cooled to 0° and the aryl diazonium borofluoride and zinc dust were added alternately. There was an immediate rise in temperature. The addition of the reagents was regulated in such a way that the temperature did not exceed 20°. After decomposition of all the aryl diazonium borofluoride (negative reaction with β -naphthol) the acetone was distilled from the reaction flask on a water bath; the residue in the flask was diluted with water and extracted several times with ether. The ether extract was washed with water to a neutral reaction and dried with calcined calcium chloride. After distillation of the ether the residue was distilled in a vacuum or with steam.

The dibromides were obtained from ether or alcoholic solution of the diaryl selenides by addition of bromine.

Diphenyl selenide and diphenyl diselenide. From 13.35 g (0.06 mole) of $SeCl_4$ and 23.2 g (0.12 mole) $C_6H_5N_2BF_4$ and 7.9 g (0.12 mole) of Zn dust after distillation in a vacuum we obtained the following fractions (p = 5 mm): I, up to 110° 0.76 g; II, 133-158° 4.74 g; III, 178-210° 3.73 g; fraction I consisted of condensation products of acetone; fraction II was diphenyl selenide which on repeated distillation in a vacuum boiled at 128-132° (4 mm). The literature give [5]: b.p. 159° (10 mm). Yield 33% of theory. From a solution of 0.5 g of diphenyl selenide in alcohol we obtained 0.5 g of the dibromide (yield 66% of theory) with m.p. 143-144° (crystallized from alcohol). The literature [6] gives m.p. 140°; 144° [7]. From fraction III by repeated distillation we obtained a further amount of diphenyl selenide with b.p. 130-145° (3 mm), and from the fraction with b.p. 170-180° (3 mm) we isolated 0.06 g of diphenyl diselenide with m.p. 61° (crystallized from alcohol). The literature gives 62.5° [8], 63° [9]. We obtained the tetrabromide with m.p. 101-102° (from ether) and the double salt with

mercuric chloride with m.p. 182-184° (from acetone). The literature gives for the m.p. of the tetrabromide 111° [8], for $(C_6H_5)_2Se_2 \cdot 2HgCl_2$ 187-188° [9].

Di-p-tolyl selenide was obtained from 27 g (0.13 mole) p-$CH_3C_6H_4N_2BF_4$, 14.55 g (0.065 mole) of $SeCl_4$, and 8.5 (0.13 mole) of Zn dust; yield 1.75 g (10.3% of the theory); m.p. 68-69° (from alcohol). The literature gives 69-69.5° [10]. Dibromide m.p. 157-158° (from benzene). The literature gives 162° [10].

Di-o-tolyl selenide was obtained from 36 g(0.174 mole) o-$CH_3C_6H_4N_2BF_4$, 19.9 g(0.087 mole) $SeCl_4$, and 11.3 g (0.171 mole) Zn dust; yield 0.97 g (4.2% of theory), m.p. 61-62° (from methanol). The literature gives m.p. 61-62° [10]; dibromide has m.p. 81° (with decomposition). The literature gives m.p. 84° (with decomposition) [10].

Di-p-methoxyphenyl selenide was obtained from 32.05 g (0.14 mole) p-$CH_3OC_6H_4N_2BF_4$, 15.8 g (0.07 mole) $SeCl_4$, and 9.5 g (0.14 mole) Zn dust; yield 0.64 g (3% of theory); m.p. 55-56° (from alcohol). Literature gives m.p. 56-57° [11]. Dibromide has m.p. 120-122°. The literature gives m.p. 118-119° [11].

Di-p-chlorophenyl selenide was obtained from 25.5 g (0.112 mole) p-$ClC_6H_4N_2BF_4$, 124 g (0.06 mole) $SeCl_4$, and 7.3 g (0.11 mole) Zn dust; yield 2.59 g (15.8% of theory); m.p. 96-97° (from alcohol). The literature gives m.p. 95-96° [12]. Dibromide, m.p. 136-138° (not recrystallized); analysis of the unrecrystallized substance: $C_{12}H_8Br_2Cl_2Se$. Found: Br 31.97; 32.22%. Calculated: Br 34.59%.

SUMMARY

By decomposition of aryl diazonium borofluorides with powdered zinc in the presence of selenium tetrachloride in acetone we have obtained diaryl selenides with aryls: phenyl, p- and o-tolyl, p-chlorophenyl, and p-methoxyphenyl.

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THE REACTIONS OF TRIMETHYLSILOXYTRICHLOROTITANIUM WITH ALCOHOLS

K. A. Andrianov and N. V. Delazari

Institute of Organic Chemistry of the Elements, Academy of Sciences, USSR

The first representative of the trimethylsiloxyalkoxytitaniums was obtained in the esterification of bis-(trimethylsiloxydichloro)titanium by butyl alcohol [1]. The reaction of trialkylhydroxysilanes with titanium tetrachloride led to the preparation of tetrakis-(trimethylsiloxy)titanium [2] and tetrakis-(triphenylsiloxy)-titanium [3] or to obtaining a mixed tetrakis-(diphenylmethylsiloxy)titanium [4]. In study of the reaction of trimethylsiloxytrichlorotitanium with butyl alcohol and with diphenylmethylhydroxysilane it was found that the reaction of replacement of the chlorine on the titanium by butoxy or diphenylmethylsiloxane groups was accompanied by side reactions. As experiments showed, trimethylsiloxytrichlorotitanium and butyl alcohol (in equimolecular amounts with a 20% excess of butanol and with neutralization of the hydrogen chloride by ammonia) react with formation not of trimethylsiloxytributoxytitanium, but of tetrabutoxytitanium.

The formation of tetrabutoxytitanium shows that along with replacement of the chlorine by butoxy groups there is also an exchange reaction of the trimethylsiloxy group, which is connected with the titanium, by the butoxy group. The chemical process can be expressed by the following reactions:

a) $\quad (CH_3)_3SiOTiCl_3 + 3C_4H_9OH \xrightarrow{\ NH_3\ } [(CH_3)_3SiOTi(OC_4H_9)_3] + 3NH_4Cl$

b) $\quad [(CH_3)_3SiOTi(OC_4H_9)_3] + C_4H_9OH \longrightarrow$

$$(CH_3)_3SiOH + Ti(OC_4H_9)_4$$
$$\downarrow$$
$$(CH_3)_3SiOSi(CH_3)_3$$
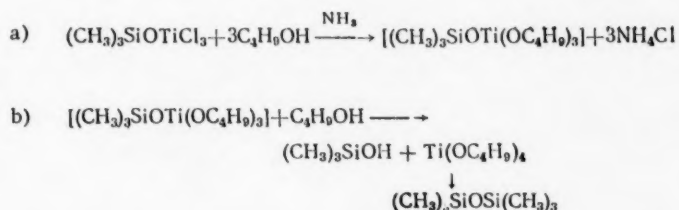
The exchange of the trimethylsiloxy group on the titanium with the butoxy group under the influence of butyl alcohol in trimethylsiloxytrichlorotitanium proceeds easily at temperatures which do not exceed 70°.

The reactivity of the trimethylsiloxy group in trimethylsiloxytrichlorotitanium is shown to be very great not only by the action on it of butyl alcohol, but also in the reaction of trimethylsiloxytrichlorotitanium with diphenylmethylhydroxysilane. When a benzene solution of trimethylsiloxytrichlorotitanium is heated with diphenylmethylhydroxysilane at 40° and ammonia is passed in, there is formed tetrakis-(diphenylmethylsiloxy)titanium. The reaction of formation of tetrakis-(diphenylmethylsiloxy)titanium can be represented as follows: (see scheme on next page).

The compound obtained in the first reaction, tetrabutoxytitanium, and that in the second, tetrakis-(diphenylmethylsiloxy)titanium, were identified by chemical analysis. Also, determination of the infrared spectra in these compounds showed that in tetrabutoxytitanium absorption did not occur in the region 916-920 cm^{-1} which shows the absence of the Ti-O-Si group, and tetrakis-(diphenylmethylsiloxy)titanium showed an intense band at 916-920 cm^{-1} (which is determined by oscillation of the Ti-O-Si group).

a) $(CH_3)_3SiOTiCl_3 + 3(C_6H_5)_2CH_3SiOH \xrightarrow{NH_3} (CH_3)_3SiOTi[OSi(C_6H_5)_2CH_3]_3 + 3NH_4Cl$

b) $(CH_3)_3SiOTi[OSi(C_6H_5)_2CH_3]_3 + (C_6H_5)_2CH_3SiOH \longrightarrow$

$\longrightarrow [(C_6H_5)_2CH_3SiO]_4Ti + (CH_3)_3SiOSi(CH_3)_3.$
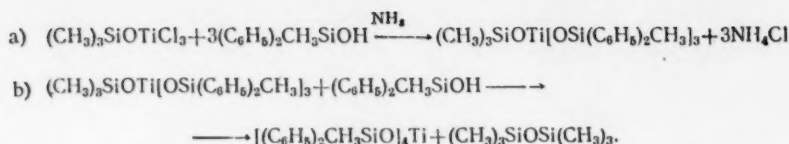
EXPERIMENTAL

Reaction of trimethylsiloxytrichlorotitanium with butyl alcohol. In a 250 ml three necked flask fitted with a stirrer, dropping funnel, reflux condenser, and tube for bubbling in ammonia was placed 19.3 g (0.2608 M) of butyl alcohol, distilled between 117-118°, in 60 ml of dry benzene. Then the flask was placed in an ice bath and when cooled to 2-5° trimethylsiloxytrichlorotitanium [b.p. 65-66° (4 mm)] was added slowly with continuous stirring from the dropping funnel in the amount of 17.7 g (0.0725 M) in 100 ml of dry benzene. A white precipitate of NH_4Cl came down. Ammonia was passed for a further 1.5 hours at 10-12°, and then the reaction mass was heated at 40-60° for two hours. The precipitate was filtered off, the benzene was distilled using a water pump. The residue of 17.8 g was distilled with an oil pump. We isolated a product with b.p. 176-177° (8 mm); 10.57 g (40.2% of the theory). Found: C 56.66; H 10.50; Ti 14.18%. $(C_4H_9O)_4Ti$. Calculated: C 56.30; H 10.58; Ti 14.36%.

Reaction of trimethylsiloxytrichlorotitanium with diphenylmethylhydroxysilane. In a 250 ml three necked flask fitted with a stirrer, dropping funnel, reflux condenser and tube for bubbling in ammonia was placed 10.45 g (0.0488 M) of diphenylmethylhydroxysilane in 100 ml of dry benzene. With cooling and in a stream of ammonia we added dropwise 3.62 g (0.0148 M) of trimethylsiloxytrichlorotitanium in 70 ml of dry benzene. At first a yellow precipitate came down, which changed to white. After precipitation of the ammonium chloride, ammonia was passed for another 0.5 hours the mixture was heated for two hours at 25-30°, and stirred at room temperature for three hours. The precipitate was centrifuged off, the benzene was distilled, and the flask residue was fractionated. We obtained a product with b.p. 346-348° (3 mm), 3.38 g (25.4% of theory); n_D^{21} 1.5988; d_4^{20} 1.1394; Found: MR 272.48; Calculated: MR 274.80; Found: C 69.23; H 6.07; Si 12.34; Ti 5.21%. $C_{52}H_{52}O_4Si_4Ti$. Calculated: C 69.40; H 5.78; Si 12.51; Ti 5.33%.

SUMMARY

1. In the reaction of trimethylsiloxytrichlorotitanium with butyl alcohol there is an exchange reaction of replacement of the trimethylsiloxy group by the butoxy group.

2. The reaction of trimethylsiloxytrichlorotitanium with diphenylmethylhydroxysilane leads not to trimethylsiloxytri-(diphenylmethylsiloxy)titanium, but to tetrakis-(diphenylmethylsiloxy)titanium.

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STUDY OF THE REACTION OF PYRIDINE WITH ETHYL IODIDE
IN n-PROPYL AND n-BUTYL ALCOHOLS AT PRESSURES UP TO
2000 kg/cm²

M. G. Gonikberg and B. S. El'yanov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

We have reported previously on the results of a study of the reaction of pyridine with ethyl iodide in acetone, ethyl alcohol, nitrobenzene, and cyclohexanone [1-4]. We concluded from these investigations that in this reaction the activated complex is solvated much more weakly than the ion of iodine and N-ethylpyridine. The present work was carried out to widen further the solvents studied in checking this conclusion for errors.

EXPERIMENTAL

The method of preparation and constants of the pyridine and ethyl iodide were given in [2] n-propyl alcohol, "purified for laboratory work" grade, was made absolute with calcium oxide, then with calcium, and was distilled and fractionated in a rectifying column. We took the fraction with b.p. 97.1-97.2° (760 mm), d_4^{20} 0.8035; n_D^{20} 1.3856. n-Butyl alcohol was made absolute with magnesium, distilled and fractionated in a rectifying column; b.p. 117.7-117.8°, n_D^{20} 1.3992.

The kinetic measurements were carried out by the method described previously [1] at a temperature of $50 \pm 0.1°$ and pressures of 1500, 1000, and 2000 kg/cm². The initial concentrations of pyridine and ethyl iodide were about 0.5 M. In studying the reaction kinetics in n-propyl alcohol we determined the concentration of pyridine during the course of the reaction [2]. We also carried out two kinetic experiments at pressures of 1 and 500 kg/cm² using the method of analysis described [4] (titration of the iodide). Both methods of analysis gave agreeing results (see below) but the second method was more accurate and therefore it was taken for the study of the reaction in n-butyl alcohol.

The conductivity of solutions of N-ethylpyridinium iodide was measured at $50 \pm 0.05°$ on an MM3CH-55 conductometer at four concentrations of the salt, from $2.5 \cdot 10^{-4}$ to 0.25 M in n-propyl alcohol and from $1 \cdot 10^{-4}$ to 0.1 M in n-butyl alcohol.

The volume effect in the reaction (ΔV) was measured with a pyknometer as follows: 1 M (at 20°) solutions of pyridine and ethyl iodide in a 100 ml calibrated flask were cooled in ice water, poured together, and part of the resulting solution was poured into a 60 ml pyknometer and the remaining solution was placed in a thermostatically controlled vessel with a reflux condenser at 50°. After keeping in the thermostat at $50 \pm 0.02°$ the pyknometer was quickly cooled to room temperature, weighed, and then the concentration of N-ethylpyridinium iodide was determined. As the reaction proceeded the vessel with the solution was taken from the thermostat, cooled in ice water and again we determined its specific gravity and concentration of N-ethylpyridinium iodide. The calculation of ΔV was carried out in the same way as in [3].

Treatment of the results of the kinetic measurements of the reaction in n-propyl alcohol was the same as

we described in [2]. In the construction of the graph in the coordinates $\ll (1)/(b-x)+B, \tau''\gg$ [*] for the reaction in n-butyl alcohol instead of a straight line corresponding to a bimolecular reaction we obtained a curve convex to the abscissa. This fact evidently depends on the presence of an autocatalytic reaction [5] which proceeds side by side with the main one. It was shown that in the experiments carried out at atmospheric pressure and at 500 kg/cm^2, x was a linear function of time, and at higher pressures this function varied only somewhat from linearity (basically, the linear relation by x to τ can occur only in a limited interval of the degree of transformation.) This fact permits us to determine graphically the value of $dx/d\tau$ at $\tau = 0$ and to calculate the rate constant of the noncatalytic reaction studied by the equation

$$k = \left(\frac{dx}{d\tau}\right)_{\tau \to 0} \cdot \frac{1}{ab}.$$

In Table 1 we give the values for the rate constant of the reaction in ethyl[2] n-propyl, and n-butyl alcohols, and also the values of $\Delta v^{\neq}$, the change in volume in the formation of one mole of activated complex from the starting substances, calculated by the equation of Evans and Polanyi [6].

TABLE 1

Results of Kinetic Measurements in Alcohols

P in kg/cm^2	Ethyl alcohol		n-Propyl alcohol		n-Butyl alcohol	
	$k \cdot 10^4$ in liter · mole^{-1} x min^{-1}	$\Delta v \neq$ in cm^3 · mole^{-1}	$k \cdot 10^4$ in liter · mole^{-1} x min^{-1}	$\Delta v \neq$ in cm^3 · mole^{-1}	$k \cdot 10^4$ in liter · mole^{-1} x min^{-1}	$\Delta v \neq$ in cm^3 · mole^{-1}
1	8,80	—27,8	6,92*	—24,1	5,36	—24,9
500	13,2	—22,6	9,95*	—21,4	7,88	—21,3
1000	18,7	—19,1	14,3	—19,6	11,0	—18,0
2000	32,8	—14,9	26,0	—16,4	18,6	—14,0

[*] In carrying out the experiments with analysis of iodide we obtained rate constants of $7.00 \cdot 10^4$ at 1 kg/cm^2 and $10.1 \cdot 10^4$ at 500 kg/cm^2.

TABLE 2

Results of Measurement of ΔV and λ in Alcohols

	Ethyl alcohol		n-Propyl alcohol		n-Butyl alcohol	
x in mole · liter^{-1}	0,15	0,18	0,055	0,12	0,058	0,091
ΔV in cm^2 · mole^{-1}	40	39	37	36	33	33
λ	26,6	25,2	11,7	10,8	5,8	5,7
α	0,19	0,18	0,16	0,14	0,095	0,093

For calculation of the rate constants we used the data in the literature on compressibility of n-propyl [7] and n-butyl alcohol [8].

Calculation of n, the upper limit for the number of molecules of solvent which solvate the activated complex [3], gave a value of 0.8 in n-propyl alcohol and 1.1 in n-butyl alcohol. In Table 2 we give values for ΔV, the change in volume in the reaction, λ, the equivalent conductivity, and α, the degree of dissociation of N-ethylpyridinium iodide in n-propyl and n-butyl alcohols from the results of the present work, and also for ethyl alcohol from the results of [3].

As tables 1 and 2 show, the rate constants, degree of dissociation, and change in volume for the reactions decrease with increasing molecular weight of the alcohol used as the solvent.

It was shown previously [3] that the problem which interests us of the comparison of solvation of activated complex and ions of the reaction product can be solved by comparison of the volume effects of the solvation of the activated complex, $\Delta_2 v^{\neq} = \Delta v^{\neq} - \Delta_1 v^{\neq}$ and $\Delta V_s - \Delta V_0$, where $\Delta_1 v^{\neq}$ and ΔV_0 are the values for the change in

[*] b is the initial concentration of ethyl iodide; x the concentration of N-ethylpyridinium iodide at the moment of time τ; $B = (b-a)/2[(1/(b-x)^2)-1/b^2]$, where a is the initial concentration of pyridine.

volume in the absence of solvation respectively for the activated complex and for the reaction product. According to [4] $\Delta_1 v^{\neq} = 20$ cm^3/M and the value for $\Delta V_0 = -22.5$ cm^3/M. Then the value of $\Delta_2 v^{\neq}$ will be 4.1 cm^3/M in n-propyl alcohol and -4.9 cm^3/M in n-butyl alcohol. The corresponding values for ΔV_s are -14 cm^3/M and -10.5 cm^3/M. It is evident from these results that in each solvent the value of $\Delta_2 v^{\neq}$ in absolute size is less than the size of ΔV_s. At the same time the volume effect of the solvation of the iodide ion and N-ethylpyridinium ion should be more in absolute size than the value of ΔV_s which includes the volume effect of solvation both of the ions and the undissociated molecule. Since the degree of dissociation of N-ethylpyridium iodide in both studied alcohols is not great, it is clear from this discussion that the earlier conclusion that the activated complex is much more weakly solvated than the ions of the reaction product is also confirmed by running the reaction in n-propyl and n-butyl alcohols.

SUMMARY

1. The rate constants for the reaction of pyridine and ethyl iodide in a series of solvents, ethyl alcohol, n-propyl alcohol, and n-butyl alcohol are decreased at each pressure studied. In the same order there is decrease in degree of dissociation of the N-ethylpyridinium iodide and the change in volume of the system in the reaction in these solvents.

2. These results of the investigation of the reaction of pyridine with ethyl iodide in the solvents studied confirm the previous conclusion that the activated complex is solvated much more weakly than the ions of the reaction product.

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THE ELECTROPHYLIC AND RADICAL SUBSTITUTION OF
THE MERCURY ATOM BY IODINE IN MERCURY-ORGANIC SALTS

O. A. Reutov and I. P. Beletskaya

The M. V. Lomonosov Moscow State University

In the course of an investigation of the mechanism of electrophylic substitution at a saturated carbon atom we have studied the reaction of mercury-organic salts with iodine. The salts used were the ethyl ester of α-bromomercuryphenylacetic acid (I) and benzylmercurybromide (II). The electrophylic substitution of the mercury atom was carried out by the action of iodine in a solution of cadmium iodide. The reaction was carried out in aqueous

dioxan and can be represented by $R - HgBr + J_2 \xrightarrow{\quad CdJ_2 \quad} R - J + HgBrJ.$

In the case of substance (I) the reaction proceeds instanteously, but in the case of substance (II) considerably more slowly. We have investigated the kinetics of the reaction of substance (II) by two methods: spectrophotometrically and titrimetrically, and have established the total order as 2 (first order with respect to each of the components). In the absence of cadmium iodide, the reaction proceeds instantaneously by a photochemical process, according to a radical mechanism. The reaction of substance (I) with iodine in the absence of cadmium iodide (the radical reaction) is of first order with respect to iodine and zero order with respect to the mercury-organic salt. The kinetics have been obtained by a spectrophotometric method.

We have thus established the important effect of the structural factor of the rate of electrophylic and radical reactions for the substitution of the mercury atom at a saturated carbon atom by an iodine atom.

THE INTRODUCTION OF DICHLOROCARBENE INTO THE METAL HALOGEN BOND

O. A. Reutov and A. N. Lovstova

The M. V. Lomonosov Moscow State University

We have found that dichlorocarbene, which is formed through the reaction of potassium tertiary butylate on chloroform in a benzene solution, is capable of introduction into the mercury-chlorine bond with the formation of trichloromethylmercury organic compounds.

Mercuric chloride reacts with dichlorocarbene, with the formation of trichloromethylmercurychloride (m.p. 180°). Published data give m.p. = 173° [1]. The mercury content found = 56.83%; the calculated value is 56.60%.

$$Cl—Hg—Cl + :CCl_2 \longrightarrow CCl_3—Hg—Cl$$

Phenylmercury chloride forms trichloromethylphenylmercury (m.p. = 113.5-114°). The published data give: m.p. 144-116° [2].

$$C_6H_5—Hg—Cl + :CCl_2 \longrightarrow C_6H_5—Hg—CCl_3$$
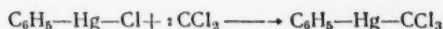
Trans-β-chlorovinylmercurychloride forms trichloromethyltrans-β-chlorovinylmercury (m.p. = 80-81°). The mercury content = 53.06%; the calculated value = 52.72%.

$$ClCH=CH—Hg—Cl + :CCl_2 \longrightarrow ClCH=CH—Hg—CCl_3$$
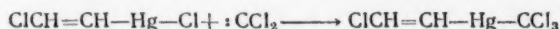
The last compound, on treatment with chlorine or bromine is converted into trichloromethylmercurychloride and trichloromethylmercury bromide respectively:

$$ClCH=CH—Hg—CCl_3 \begin{array}{c} \xrightarrow{Cl_2} CCl_3—Hg—Cl + ClCH=CHCl \\ \xrightarrow{Br_2} CCl_3—Hg—Br + ClCH=CHBr \end{array}$$
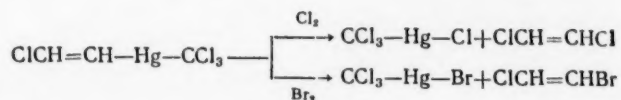
We are at present studying the possibility of synthesizing trichloromethyl organometallic compounds by other methods using dichlorocarbene.

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INTERACTION OF 2-FORMYLCYCLOALKANONES
WITH HYDROGEN PEROXIDE

L. P. Vinogradova and S. I. Zav'yalov

We have shown that when hydrogen peroxide interacts with cold 2-formylcyclopentanone and 2-formyl-cyclohexanone, these are submitted to oxidative breakdown and give the corresponding adipic and pimelic acids.
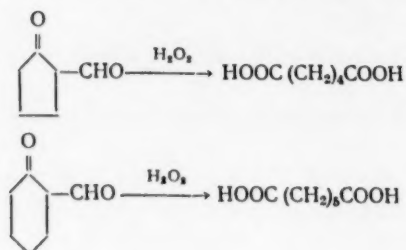
This usual reaction ot the 2-formylcycloalkanes may be used to obtain various dicobsylic acids, starting from cyclic ketones.

ANNUAL GENERAL CONFERENCE OF THE DIVISION OF CHEMICAL
SCIENCES, ACADEMY OF SCIENCES OF USSR, FEBRUARY 23, 1960

During the course of the year, the period of office of the Bureau of the Division of Chemical Sciences, which commenced in 1957, came to its close. In consequence, it was the task of the Annual General Conference of the Division, when it met on February 23 in the Conference Hall of the N. D. Zelinskii Institute of Organic Chemistry, to receive an account of the activities of the Bureau of the Division for the three years now expiring, and to carry out the election of the new members of the Bureau of the Division, in addition to its normal annual review of the fundamental attainments in science within the scope of the Division.

In view of the illness of Academician N. N. Semenov, Academician-Secretary of the Division, the report was presented by the first assistant Academician-Secretary, Academician A. P. Vinogradov. The report gave primary attention to an analysis of the fulfilment of the resolutions of the previous General Conference of the Academy of Sciences of USSR referred to in a communication by Vice-President of the Academy of Sciences of USSR A. V. Topchiev, entitled "The 21st Convention of the Communist Party of the Soviet Union, and the Tasks of Soviet Science". According to these resolutions, attention was to be concentrated, and all available forces and means employed for the purpose, on an active prosecution of research on matters of basic scientific importance. Within the field of chemistry, this involved primarily the chemistry of compounds of high molecular weight, the chemistry of natural and biologically active substances, the chemistry of the rare elements, problems on the application of isotopes and radiation methods in chemistry and chemical technology, the chemistry of semiconducting materials and of chemical current sources, and the theories of chemical structure and reactivity.

In analyzing the state of theoretical and practical researches in the field of polymer chemistry, the contributor called attention to the positive influence which the resolution of the May Plenary Session of the Communist Party of the Soviet Union had exerted on the development of research in this field. He also emphasized, however, that unless there was resolute harnessing of the whole of chemical science to this end, there could be no expectation of further significant success in this branch. In the period now reported on, the number of scientific workers engaged in the chemistry, physics and physical chemistry of polymers in the institutes of the Division had increased about threefold. There had been a considerable development of the working front, not only in the institutes of the Division, but also in a number of branch institutes, in the Republican Academies, and also in associated institutes with which closer links had been established. In each of a number of directions definite progress has been made: thus, in the Institute of Elemento-Organic Compounds a new method has been worked out for the synthesis of linear polymers (the polyrecombination reaction), and a new type of polymer (the polyarylates) has been synthesized. A method has been developed for modification of the properties of polymers by activation of a surface and grafting of vinyl monomers on to it. As a consequence of a great development of research into the synthesis and study of the structure of polymers containing inorganic principal chains, polymers have been created and introduced into industry which possess a range of valuable properties. New ways of synthesizing a number of monomers have also been developed.

Success has been achieved in the Institute of High Molecular Weight Compounds in the field of the creation of transparent, thermally stable high molecular weight materials; new kinds of organic glass have been made; and new methods of synthesis have been developed for polymerized materials having high thermal stability. On the basis of investigations of the mechanism of ionic, radical and catalytic polymerisation and copolymerization of

dienes and olefins, new polymers have been obtained, which included regular and stereospecific polymers. New ion exchange resins possessing high selectivity have been synthesized. The results of work on the sorption of antibiotics may well be of basic importance for the industrial isolation of antibiotics. New data have been obtained on the structure of cellulose and cellulose hydrate fibres, and new cellulose esters have been synthesized. In the Institutes of Petroleum Chemical Synthesis and Chemical Physics, fundamental developments have been brought about by research directed to the solution of concrete scientific-technical problems on the production and modification of important synthetic materials (such as polypropylene, polyformaldehyde and polyolefines in general). Studies on the synthesis and investigation of a range of high molecular weight compounds possessing unusual electrophysical properties have proved of interest: these investigations have also been carried out in the Institutes of Elemento-organic Compounds and of Electrochemistry. Research has been commenced, and the first successes have already been achieved, into the study of polymeric coating materials in the Institute of Physical Chemistry, and on inorganic polymers in the Institutes of General and Inorganic Chemistry, and of Silicate Chemistry.

The communication referred also to most important achievements which have been realized in Institutes which are not part of the Chemical Division (such as the Institute of Polymer Chemistry of the Academy of Sciences of the Uzbek SSR, and the Institute of Chemistry of the Georgian SSR, amongst others). At the same time it was pointed out that coordination of researches on this important problem was practically non-existent. Scientific discussions on the problem had hardly been worked out at all.

In the field of the chemistry of natural and biologically active compounds, the most significant fact has been the creation of an institute, though this, unfortunately, was still in the stage of being organized. The unique importance of the problem emphasizes the necessity of taking decisive measures to accelerate the completion of the reconstruction of knowledge, and the completing of the reorganization period. The speaker also emphasized that the creation of the Institute of the Chemistry of Natural Compounds ought not to be taken to imply any intention that work on this problem in other Institutes was to be restricted. He also made reference to interesting results which had been obtained on the problem in other institutes, including: Organic Chemistry, Elemento-Organic Compounds, the Institute of Chemical Physics, and the Kazan' branch of the Academy of Sciences of USSR. A hopeful sign was the opening up of scientific consultation on the problem, and also the establishment of a close link on this matter with the leading scientists of the Czechoslovakian Peoples' Republic.

The speaker said that the preparation of ultra-pure substances and the study of their properties constituted one of the most serious problems of contemporary chemistry. Considerable progress had been made in improving the coordination of research carried out on problems of the chemistry of semiconducting materials and electrochemical sources of current, within the institutes of the Division. New compounds possessing high sensitivity in the infrared spectral region have been synthesized in the Institute of General and Inorganic Chemisty, and in the recently established Laboratory of Physico-Chemical Analysis of Semiconductors. New methods of very high sensitivity for the analysis of very pure substances have been developed in the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry. The speaker also called attention to the fact that, up to now, the institutes of the Division had not succeeded in solving the problem of obtaining certain ultra-pure substances, of which quartz was an example. The Institute of Electrochemistry had succeeded in furthering the work on the creation of fuel elements, working on the basis of important theoretical research. One of the most important tasks in dealing with the problem of the chemistry of the rare elements was the study of the physicochemical properties of various compounds of these elements with a view to discovering new fields in which they might be employed. It was important to proceed with the current successful development-work directed towards the creation of new and economical methods of obtaining the rare elements and their compounds, as well as towards the development of new analytical methods. Important results have been obtained in these fields in the Institute of General and Inorganic Chemistry, the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, and also in the Ural and Kola branches of the Academy of Sciences of USSR.

The speaker proceeded to an analysis of the problems which have arisen for science in connection with the widespread exploitation of atomic energy, isotopes and irradiation for peaceful purposes, and pointed out suitable directions which research might take, in addition to giving an account of the most important attainments in this field in the V. G. Khlopin Radium Institute, and in the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, the Institute of Physical Chemistry, the Institute of Chemical Physics and the Institute of Petroleum Chemical Synthesis. Research is being carried out in all the institutes of the Division on the problem of "The Theory of Chemical Structure and Reactivity". During the last year there has been a considerable enlarge-

ment of the application of physical methods of investigation. In addition to this, widespread use has also been made of all the forms of optical spectroscopy, and of the method of electronic paramagnetic resonance. A beginning has been made with the application of quadrupole resonance. X-ray analysis has continued, as formerly, to be widely used, together with mass spectroscopy and mass spectrometry. Amongst the methods involving the use of isotopes, the most widely used have been those involving nitrogen and hydrogen isotopes. Nuclear magnetic resonance has not been put into operation up to the present, and only slight use has been made of relaxation methods for the study of rapid chemical reactions. A large step forward in the organization and coordination of research on the problem of "The Theory of Chemical Structure and Reactivity" has been made in the scientific consulting body organized by Academicians V. N. Kondrat'ev and M. I. Kabachnik. Investigations of surface phenomena have been carried out on a wide front in the Institute of Physical Chemistry, and have led to the production of a number of important results, from both practical and theoretical points of view. Work on geochemistry and hydrochemistry has been pursued successfully in the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, the Institute of Radium and the Institute of Hydrochemistry.

The communication paid great attention to the question of the organization of introductions. During the last year the number of works passed on to industry for experimental industrial trial and introduction increased considerably. The field of the institutes' activity needs special attention. The more energetically scientific workers and leaders in the institutes devote themselves to the arrangement and carrying out of experimental industrial operations, the more rapidly and successfully will the achievements of science be exploited in the life of the nation.

The speaker, in the course of emphasizing the peculiar importance of the coordination of scientific investigations, observed that the activities of the Bureau of the Division in this field of work could not be regarded as sufficient. The new members of the Bureau would need to give special attention to the problems of planning and coordination of scientific research. During the period considered, the position had considerably improved with respect to the publication of scientific works. The number of published monographs had increased. The situation was still, however, as unsatisfactory as before in the matter of the publication of scientific articles in the chemical journals. In spite of the establishment of a number of new journals (among them "High Molecular Compounds" (Vysokomolekulyarnye Coedineniya) and "Radiochemistry" (Radiokhimiya)), and the considerable increase in the number of pages in a number of journals, the "expectation" date often amounted to one and a half years' delay. In our day this is quite intolerable. The speaker made known interesting information about the material provision for the institutes of the Division, about the progress of construction in the chemical institutes, about the instruction of recruits and the growth in the number of workers in the chemical institutes, and about the development of inter-science links. He mentioned the large work programs carried out by the institutes and the Bureau of the Division towards the completion of the 7 to 15 year plans for the development of science.

Those who took part in discussion about the communication were: Academicians V. I. Spitsyn, A. N. Frumkin; Correspondent Members I. P. Alimarin, B. V. Deryagin, N. M. Khavoronkov, Yu. G. Mamadeliev, O. A. Reutov; and Doctors of Science R. D. Obolentsev, A. A. Trapeznikov and V. I. Mikheeva. Those who took part pointed out inadequacies in the work of the institutes and of the Bureau of the Division. Special reference was made to the unsatisfactory position in the matter of introducing the achievements of the Institutes into industry, with the resultant creation and production of new equipment. The desirability of the creation of new journals was mentioned, the first of which should be the journal "Electrochemistry" (Elektrokhimiya).

During the evening session, the election of the Academician-Secretary of the Division and the new members of the Bureau took place. N. N. Semenov was unanimously reelected Academician-Secretary. The Assistant Academician-Secretaries appointed were Academicians A. P. Vinogradov and M. M. Shemyakin. Academicians appointed to the Bureau were: B. A. Arbuzov, M. M. Dubinin, V. N. Kondrat'ev, V. A. Kargin, M. I. Kabachnik, I. V. Tananaev, A. N. Terenin and A. N. Frumkin; together with Correspondent Members of the Academy of Sciences of USSR I. P. Alimarin and N. M. Khavoronkov. In accordance with the Statute of the Academy of Sciences, the resolutions of the general conference were presented to members of the Chemical Division selected on behalf of the Siberian Division from among the Correspondent Members working in the field of Chemistry: G. B. Bokii, G. K. Boreskov, V. V. Voevodskii, N. N. Vorozhtsov, A. A. Koval'skii and A. V. Nikolaev. Because of the expiration of their authority, the following directors of institutes were reelected: Academicians A. P. Vinogradov, N. N. Semenov, V. I. Spitsyn, I. I. Chernyaev, and Correspondent Members of the Academy of Sciences of USSR O. A. Alekin and V. M. Vdovenko. In addition to these, a director was chosen for the recently founded Institute of the Chemistry of Natural Compounds, and the office was awarded to M. M. Shemyakin.

GRAND GENERAL CONFERENCE OF THE DIVISION OF CHEMICAL SCIENCES,
ACADEMY OF SCIENCES OF USSR, APRIL 20-21, 1960

The Grand General Conference of The Division of Chemical Sciences was held on April 20-21, the Conference being dedicated to the ninetieth anniversary of the birth of Vladimir Il'ich Lenin.

In opening the Conference, Academician-Secretary N. N. Semenov remarked in his introductory words that V. I. Lenin figured in world history as the greatest thinker and reviver in human society. The richness of Lenin's ideas on fundamental philosophical questions of natural science would be difficult to overestimate. V. I. Lenin's classical work, "Materialism and Empirical Criticism", has honorably withstood the test of time. The works of Lenin, said N. N. Semenov, exercised their influence on the destiny of science just at the point of time when physics was beginning to penetrate into the microcosm of atoms, molecules, and electrons, and was proceeding to the reconstruction of a number of basic concepts within this field of study. Lenin showed that the revolution in physics amounts to a brilliant confirmation of the dialectical materialistic doctrine, and the new successes of physics are themselves an enrichment of dialectical materialism, having received powerful exposition in the works of V. I. Lenin, and having become the methodological basis of the current development of the science.

N. N. Semenov called attention to the part played by V. I. Lenin in the organization of Soviet science in the period from 1918 to 1924, when firm foundations were laid for the vigorous development of science in USSR during our days. In the difficult years of economic confusion during the period of the civil war, there were founded in Petrograd and Moscow the first Soviet scientific and research institutes operating in the major branches of science. Lenin understood clearly that it was necessary to secure a rapid development of the fundamental sciences on a wide front, so that this could become the theoretical foundation of the technology and industry to come in the great socialist country. Lenin always demanded a close link between theory and practice, and when he expanded the Academy of Sciences, he set before it great tasks of importance to the public economy. Soviet scientists were given every opportunity to reveal scientific and organizational initiative, and wide horizons unfolded in front of them for the applications of the achievements of science to the benefit of their land and its population. In concluding his address, N. N. Semenov called upon Soviet scientists to be worthy successors of the work of Lenin.

The scientific contributions to the session, which were devoted to problems worked out in the institutes, were read by leading scientific chemists of the Academy of Sciences of USSR. Academician M. M. Dubinin submitted a contribution on the theme, "The Theory of the Physical Adsorption of Gases and Vapors, and the Adsorptive Properties of the Adsorbents of Various Natures and Porous Structures". The communication has been fully reprinted in the journal "Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk", no. 7 (1960). Academician V. I. Spitsyn submitted a review-contribution on the theme: "New Data on the Effect of Radioactive Irradiation of Solids, and of External Radiation on some Heterogeneous Chemical Processes". This communication has been fully reprinted in no. 8 of the same journal.

Correspondent Members of the Academy of Sciences of USSR V. G. Levich and R. R. Dogonadze submitted a paper on the theme: "The Adiabatic Theory of Electronic Transitions in a Material Medium". The authors observed that, from the standpoint of the usual assumptions about the kinetics of oxidation-reduction reactions, the study of electron exchange reactions between ions in solutions, which had been undertaken by a number of authors in recent years, was a matter of great interest.

As an example, the reaction: $Fe^{3+} + e = Fe^{2+}$, was cited. The electrostatic repulsion between similarly charged ions does not permit the ions to approach to the point of direct contact. Electronic exchange therefore occurs between ions separated by a comparatively thick layer (5-8 A) of solvent.

The author showed that the solvent plays a decisive role in the electronic transition process. Because of the inertia-nature of the movement of the heavy atoms of the solvent, which are unable to keep pace with the movement of the electron, the transition process of the electron from one ion to another takes place during a fixed polarization state of the solvent between the two ions.

The mechanism of the electronic transition appears to be somewhat different at high temperatures from that at low temperatures (in comparison with the energy of the characteristic oscillations of the solvent). The author has calculated the probabilities of the processes in question, which take the form of an Arrhenius formula, with different values of the energies of activation at high and low temperatures. The calculated absolute rates are in agreement with the experimental data with respect to their order of magnitude.

Academician A. P. Vinogradov submitted a contribution on the subject of dating by means of C^{14}. The radioactive isotope C^{14} said the author, is formed in the atmosphere under the influence of neutrons from cosmic radiation: $n_1^1 + N_7^{14}P_1^1$. The disintegration of C^{14} is accompanied by the release of beta-radiation. The surface of the earth at the present time contains 80 tons of C^{14}. The explosion of atomic, and especially of hydrogen, bombs causes the formation of C^{14}. Carbon in its present condition gives about 15 disintegrations per minute per gram of carbon. The half-life period of C^{14} is 5568 ± 30 years. After its formation, the C^{14} undergoes migration in the atmosphere, hydrosphere and biosphere together with ordinary carbon. It is thus possible, from the content of C^{14} in organic substance-wood, coal, peat, etc.-and in materials of an archaeological, paloeontological and oceanographical character, to determine the absolute age when they were formed.

Various methods of estimating the disintegration of C^{14} have been tried out in the author's laboratory. As a result of these, two apparatuses have been set up for the determination of age by C^{14} dating, using a gas proportional counter. Methods have been worked out for the combustion of the substance into carbon dioxide, and for ensuring its complete purification; methods have also been designed for obtaining pure gases such as ethane and acetylene. A special proportional counter has been constructed. The apparatus is capable of functioning automatically for 24 hours or more.

It is possible to determine the age of geological and archaeological specimens within the limits 0 to 45,000 years, or even older. The error in counting amounts to 0.8%. By the application of the method, the ages of some tens of archaeological and geological specimens have been determined. In a number of cases it is possible to compare the data obtained with well-dated archaeological excavations (such as coins), and good agreement has been obtained. It has thus been possible during the last two to three years for us to determine in the USSR, for the first time, data about the date of the last ice-age, about the dates of certain historical events, etc., by determining the C^{14} content in deposits of wood, turf, coal, mammoth wool, etc.

Correspondent Member V. V. Voevodskii presented a contribution on the application of the application of the electronic paramagnetic resonance method (EPR), to the investigation of initiation in polymerization processes. The results of a series of laboratory experiments were presented, designed to provide a direct examination of the elementary acts of initiation of polymerization processes,and an identification of the particles participating in these acts.

In investigationsof the transformation of the initiator radical into a radical of the growing polymeric chain, using the case of the initiation of the polymerization of methyl methacrylate by means of the peroxide radical of teflon, the kinetics of the formation and destruction of the latter have been studied.

The possibility of the formation of free hydrogen atoms during the initiation of polymerization, as the result of photo-transition of electrons in an aqueous medium, has been investigated. It has been shown that illumination by means of ultraviolet light of solutions of substance M in aqueous acids, frozen to 77°K (where M is Fe^{2+}, I^-, etc.), results in the formation of non-chemically bound hydrogen atoms according to the reaction: $M + H_2O + h\gamma \xrightarrow{H_2SO_4} M^+ + H\cdot + OH-$, and that this formation only ceases when the temperature is raised to 120°K. In experiments using heavy water, the formation of deuterium atoms has been demonstrated. The hypothesis that polymerization initiation in such systems is due to hydrogen atoms has thus been confirmed.

The use of complexes based on aluminum trialkyls, proposed by Ziegler is of very great practical importance for the initiation of polymerization. The structure of these complexes has been the subject of very intensive study in recent years. Investigation of such systems by the electronic paramagnetic resonance method has shown that these complexes possess clearly expressed paramagnetism which undergoes change in the course of polymerization; and that, in consequence, the polymerization process has to some degree a radical character. From the form of the electronic paramagnetic resonance spectra of the complexes, conclusions have been drawn as to the structure of these, and as to the part played in their formation by dialkyl aluminum hydride. Investigation of the electronic paramagnetic resonance spectra of various chromium oxides has shown the possibility of tracing the course of valence change in chromium during the preparation of the catalyst and during the polymerization reaction.

The example considered by the speaker of the various means of initiation of polymerization show that we are in all cases concerned either with ordinary free radicals, or with ion-radicals, or, finally, with paramagnetic compounds of the complex- and surface oxide-types. V. V. Voevodskii observed that, when initiation is not due to ordinary radicals, but to anion-radicals, complexes based on aluminum and titanium or chrome heterogeneous catalysts, the active particles are characterized not only by paramagnetism, but also by the possibility of delocalization of an unpaired electron at a sufficiently large number of bonds. The possibility exists that the increased activity of these particles is connected with this circumstance.

Correspondent Member S. N. Danilov submitted a communication on the mechanism of intramolecular oxidation-reduction reactions of organic compounds. The speaker reviewed the course (mechanism) of a small section of the simultaneous intramolecular oxidation-reduction reactions, namely the acid and hydroxycarbonyl conversion of halogeno- and hydroxycarbonyl-compounds, including the sugars.

It may be affirmed, said S. N. Danilov, that the Cannizzaro reaction does not proceed by way of esters and polyacetals, but is accomplished in the same way as the benzil rearrangement in the alkaline complex. Both these reactions consist of simultaneous intramolecular oxidation-reduction processes. The acid transformation of Favorskii α-halogenated ketones cannot be explained by means of cyclopropane grouping, or by means of ketones, etc. Even the more likely alcohol-oxide scheme of Favorskii is incapable of embracing certain observed facts concerning the course of the reaction in relation to the composition and structure of the initial halogeno-ketones. More probable schemes operating through the formation of complexes with the reagent are not yet sufficiently specific, and do not appear to explain the actual transformations.

In carrying out the conversion of α-bromaldehydes into acids, S. N. Danilov pointed to the specific influence of the hydroxides of moderately heavy metals (silver, lead and barium), which are active with respect to the halogen. It was suggested that the metallic hydroxide exerts a specific directing effect on the reaction, and facilitates the mobility of the hydroxyl group in he α-alcoholic grouping.

In recent form on the conversation of glyceryl aldehyde into lactic acid, and its chlorine derivative (2-chloro-3-hydroxypropanel) into hydracrylic acid, S. N. Danilov has expressed the view that the reduction occurs at the β-alcoholic group of the glyceryl aldehyde. The presence of the halogen in the α-position makes possible the reduction of the carbon carrying the halogenate group. The possible role of the β-alcohol oxides has been pointed out. In the light of the α- and β-transformations of the hydroxyl groups, the manner of formation of the known saccharinic acids has been considered. In the opinion of S. N. Danilov, a number of complex problems concerning the mechanism of the simultaneous oxidation-reduction intramolecular processes are still in need of further consideration.

Doctor of Chemical Science Ya. P. Gol'dfarb submitted a communication on new methods of synthesizing macrocyclic compounds. At the present time, said the speaker, macrocyclic molecules include compounds with a moderate (8 to 12 atoms) and large (13 atoms and above) ring size. New data have appeared in recent years to emphasize the important physiological part played by macrocyclic compounds, including oxytosin, certain antibiotics such as gramicidin-C, the macrolids, etc. The biological significance of the ring may lead to the loss if its specific effect. An important method for the preparation of cycloaliphatic compounds of the type indicated consists in building up the often little accessible open chains and bringing about their closure. The yield in such processes varies with change in the number of members in the chain and the method employed to bring about cyclization, but in all cases the structure of the macrocyclic compound is determined by that of the open chain, and it is difficult or practically impossible to introduce addition substituents by further treatment of the product.

A method for synthesizing macrocyclic compounds worked out by the speaker is different in principle from methods described earlier, and is based on the use of thiophene substitution products. These compounds, under the conditions of the Friedel -Crafts reaction, acyloin condensation, etc., undergo closure into bi- and tricyclic systems, with respectively two and four free positions in the thiophene rings, into which additional substituents may be introduced. Moreover, these compounds may be submitted to reductive desulfurization by means of Rinea nickel, with the production of cycloaliphatic compounds. The proportions in which the reaction products appear depends on the nature of the medium in which the condensation is carried out. Other means also exist for the preparation of macrocyclic compounds including the thiophene ring, the basis of which involves the geometrical peculiarities of the latter.

At the conclusion of the session Academician N. N. Semenov took part with a contribution on the problem of the improvement of scientific propaganda. N. N. Semenov, in analyzing the state of the problem of scientific propaganda in the Academy of Sciences, and especially in the Chemical Division, called upon the scientists of the Division to treat the problem with great attentiveness, and especially to write more popular scientific books and articles, as well as to take an active part as helpers in the Society for the distribution of polytechnic and scientific information in its various activities.

IN MEMORY OF BORIS NIKOLAEVICH DOLGOV (Obituary)

On December 6, 1959, after a grave and protracted illness, Doctor of Chemical Science, Professor Boris Nikolaevich Dolgov died.

B. N. Dolgov was born on August 14, 1894 in St. Petersburg*, the son of an art teacher. He completed his studies at the classical gymnasium in 1912, and was accepted in the Philological Faculty of the University of St. Petersburg*. In 1914, however, he transferred to the chemical branch of the Physico-Mathematical Faculty. After he was demobilized from the Red Army (in which he had served as a volunteer), Boris Nikolaevich completed his studies at the University in 1925, giving a brilliant account of himself in his diploma work on the theme "The Isomerization of Six-Membered Rings into Seven-Membered Rings", which had been performed under the direction of Academician A. E. Farovskii. For the next three years he worked as a Scientific Associate (first grade) in the Chemical Institute of the Academy of Sciences of USSR in Leningrad. Commencing in 1928, Boris Nikolaevich worked for the next eleven years on the creation from its first beginnings of the State Institute of High Pressures, first as Chief Chemist, and then as Director of the Gas Reaction Section. During this period B. N. Dolgov and a group of colleagues carried out a series of investigations of great theoretical and economic importance.

In 1938, Boris Nikolaevich was granted the degree of Candidate of Chemical Sciences without the submission of a dissertation, and some months later, after the submission of a dissertation on "The Synthesis of Alcohols from Oxides of Carbon under Pressure", was granted the degree of Doctor of Chemical Sciences and the rank of Professor. In the same year, 1938, B. N. Dolgov directed a program of work of importance for the defense of the country, because of which he was honored by a government award. In 1953 B. N. Doglov was appointed Director of the Laboratory of Silico-organic Compounds in the Institute of the Chemistry of Silicates of the Academy of Sciences of USSR, and he continued to direct this until the end of his life.

Boris Nikolaevich was an uncommonly interesting, lively and absorbing companion, and was constantly friendly, alert and cheerful. He showed great awareness of the needs of his colleagues and students, whose affection and respect he gained. B. N. Dolgov published somewhere around two hundred scientific communications in the fields of chemical catalysis and the chemistry of silico-organic compounds, working with numerous students and colleagues.

Boris Nikolaevich was widely known as the author of a Russian variant of the method for the synthesis of methanol from carbon monoxide and hydrogen under pressure, which was exploited on an industrial scale even as early as 1933. The factory is still operating on the basis of this method up to the present time. His later investigations have led to the discovery of active catalysts which have made it possible to synthesize higher alcohols also from carbon monoxide and hydrogen. This group of investigations also includes his studies of the catalysis synthesis of hydrocarbons starting with carbon monoxide and hydrogen, or with the gases obtained by the low temperature carbonization of coal, as well as the development of the catalytic method of synthesizing acetic acid from carbon monoxide and methanol, and a range of other researches.

In 1935 Boris Nikolaevich disclosed a new esterification reaction with out the use of acid, by means of the catalytic conversion of primary alcohols and esters. He also discovered subsequently both the catalysts and the

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* The Russian text has "Peterburg" here, and it is assumed that the name refers to this, in view of the association with Leningrad which follows in connection with Dolgov's activities after the revolution — Translator.

dehydrocyclization of aliphatic oxygen-containing compounds. He also investigated in detail various catalytic conversions of aliphatic alcohols, ketones and aldehydes. Many of these investigations are not only of theoretical, but also at the same time of great practical interest, combining as they do exceptional simplicity of operation of the processes, and high yields of the ultimate products. Amongst the catalytic studies of Boris Nikolaevich are also included his early works which established the regularities governing the hydrogenation under pressure of poly-arylmethane compounds, as well as the numerous investigations which he began in 1946 on the catalytic alkylation of various aromatic compounds.

The second major direction followed in the scientific researches of Boris Nikolaevich was the investigation of silico-organic compounds. He was in fact the pioneer of this branch of research in the Soviet Union. His first excursion into this field was begun as early as 1928, and he maintained his interest in these compounds to the end of his days. The studies of Boris Nikolaevich were concerned with varied questions of the catalytic conversions of organic silicon derivatives of different classes, and also with the synthesis, and the study of the mechanisms of the reactions of, various silico-organic and silico-elemento-organic compounds. B. N. Dolgov carried out the catalytic dehydrogenation of the tetraalkylsilanes, and investigated the reactions of these compounds at high temperatures under pressure, as well as in the presence of catalysts. He studied in detail the catalytic dehydro-condensation of trialkylsilanes with different amino-, hydroxy- and oxo-organic compounds, and discovered effective catalysts for this class of reactions. Numerous investigations were carried out under the directions of B. N. Dolgov on the synthesis of silico-organic compounds containing various functional groups: ethers, acids, aldehydes and others.

Boris Nikolaevich, as a true scientific communist, always coupled his scientific researches with the demands of industry and practice. Under his direction, new forms of insulation materials effective both for heat, moisture and electrcity, and of thermostable compounds within the range of silico-organic compounds were created, and many of these have been put to practical use. His research into the hydrophobization of various structural materials, of fabrics and of paper, etc., have also found application.

Boris Nikolaevich also well-known at home and abroad as the author of a range of fundamental monographs. In 1933 he wrote the first monograph in the world on "The Chemistry of the Silico-Organic Compounds", which for a long time remained the only monograph on this topic in the literature of the world. The first edition of B. N. Dolgov's book, "Catalysis in Organic Chemistry" (1949) was translated into Chinese, Polish and Czech; and the second edition, which was issued in 1959 not long before his death, is to be translated and published in the German Democratic Republic. Boris Nikolaevich also devoted much attention, force and energy to the education of scientific personnel. Many of his pupils have received the degrees of Candidate and Doctor of Science.

In the person of Boris Nikolaevich, Society science has lost a great scientist; his students have lost a brilliant lecturer and teacher; and his colleagues and pupils have lost an attentive and sensitive leader.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AĒ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy—AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)			
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1959
	Biofizika	Biophysics	National Institutes of Health*		1	1956
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1957
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Life Sciences — Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Chemical Sciences — Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Earth Sciences — Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1	1957-
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	6	1958
		Mathematics — Doklady Soviet Mathematics	The American Mathematics Society	123 / 131	6 / 1	1958 / 1961
		Physics — Soviet Physics—Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)			
Élecktrosvyaz	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		9	1959
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*	43	1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences		1	1957
Geokhimiya	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics—Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau	1	1	1952

continued

Abbreviation	Journal (transliterated)	English title	Translating organization	No.	Year
Izv. AN SSSR, Otd). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fizich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union	1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute	1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)	1	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1958
	Metallurg	Metallurgist	Acta Metallurgica	1	1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications	1	1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics	6	1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences	1	1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association	1	1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America	1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers	1	1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada	1	1957
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1959
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.	1	1959
	Stal'	Stal (In English)	Iron and Steel Institute	1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association	1	1956
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics	4	1959
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources	1	1956
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1960
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)	1	1958
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.	4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*	1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*	1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*	1	1957
Zavl(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi fiziki	Russian Journal of Physical Chemistry	The Chemical Society (London)	7	1959
ZhMÉi Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*	1	1957
ZhNKh Zh(urn). neorgan(ich). khimii	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)	1	1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*	1	1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.

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